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PHYSICAL CHEMISTRY.—*An excursion in chemical thermodynamics.*[1]

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Thermodynamics provides laws that govern the passage of energy from one system to another, the transformation of energy from one form to another, and the utilization of energy for useful work. These same laws also govern the change of matter from one molecular or atomic species to another.

All matter of specified composition, in given electrical, magnetic, and gravitational fields, may be considered to have five fundamental thermodynamic properties—pressure, volume, temperature, energy, and entropy. Knowledge of the proper manner of applying the laws of thermodynamics to these fundamental properties of substances permits one to subject all transformations of energy and matter to the powerful scrutiny of thermodynamics.

Every physical process or chemical reaction, including biological ones, may be examined thermodynamically. However, the fruitfulness of such examination depends greatly upon the extent to which are known the fundamental properties of the initial and final states of the process or reaction. If the energy and entropy are known, with respect to appropriate reference points, for all values of pressure, volume, and temperature to be covered in the investigation, then the thermodynamic examination can be a complete one.

When under given conditions a chemical reaction takes place of its own accord, it is because the ensemble of atoms and molecules has an opportunity of improving its over-all situation with regard to energy and entropy. In the final state of a naturally occurring reaction or process, the atoms become arranged in molecular forms that have a more favorable combination of lower energy and higher entropy than in the initial state.

Given certain initial and final states of a proposed chemical reaction, it is frequently desirable to ascertain, without possible costly experimentation, what will be the amounts of the reacting material in the initial and final states, respectively, at thermodynamic equilibrium under the specified conditions. With known data on the changes in energy and entropy between the two states, under the given conditions of pressure, volume, and temperature, thermodynamics permits calculation of the amounts of material in the two states at equilibrium. If the amount of the material in the final state at equilibrium is very small, the proposed reaction has an unfavorable equilibrium under the specified conditions. If the amount of the material in the final state at equilibrium is large, the proposed reaction has a favorable equilibrium under the given conditions.

Another illustration of the power of chemical thermodynamics is the following: Given 10 possible products which may be formed from one starting substance, what are the amounts of the starting substance and of each of the 10 possible products at equilibrium under the specified conditions? With a knowledge of the difference in energy and in entropy between the starting substance and each of the 10 products, one can answer this question with confidence, without experimentation on the complex reaction involved.

In the foregoing examples it is important to note that thermodynamics does not evaluate the rate at which the given equi

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librium concentrations or amounts are reached, does not specify the mechanism by which the molecules are transformed from the initial to the final state and vice versa, and does not disclose any information regarding the details of the molecular structure of the molecules involved in the reaction.

The rate at which molecules pass from the initial state to the final state, and vice versa, in a given chemical reaction is determined by the energy of activation and the temperature. The rate of a specified reaction increases with increase in temperature and with decrease in the energy of activation. By means of a suitable catalyst, the energy of activation can be very materially reduced, producing a correspondingly large increase in the rate of reaction. The function of a catalyst is primarily twofold—to increase the rate of reaction and to guide the reaction along the desired course.

ENERGY AND THE FIRST LAW OF THERMODYNAMICS

There exists a property of every thermodynamic system called its energy, E, which is characterized by the fact that it is fully conserved over all systems in every process. The existence of energy is manifested to us through observations of the changes which it produces in material things. The various kinds of energy with which we are familiar include heat energy, mechanical kinetic energy, mechanical potential energy, electrical energy, and radiation energy.

Different processes have associated with them quite appreciably different amounts of energy. The following examples illustrate the tremendous variation in the magnitude of the changes in energy which accompany different processes:

Processes involving changes in the nuclei of atoms.—In the nuclear fission of uranium 235 with 1 neutron to form barium, krypton, and 3 neutrons,

$$U^{235} + n^1 = Ba + Kr + 3n^1, \quad (1)$$

the energy given up by the system to the surroundings is approximately 4×10^{12} cal/mole.

Processes involving changes in the valence electrons of atoms or molecules.—In the recombination of an electron with a proton to form a neutral hydrogen atom,

$$\theta + H^+ = H, \quad (2)$$

the energy given up by the system to the surroundings is about 3×10^5 cal/mole.

Processes involving changes in molecular structure.—In the reaction of hydrogen with oxygen to form water,

$$H_2 + \tfrac{1}{2} O_2 = H_2O \quad (3)$$

the energy given up by the system to the surroundings is about 6×10^4 cal/mole.

Processes involving changes of state, as from solid to liquid or liquid to gas.—In the condensation of water vapor to liquid water,

$$H_2O \text{ (gas)} = H_2O \text{ (liquid)}, \quad (4)$$

the energy given up by the system to the surroundings is about 1×10^4 cal/mole.

Processes involving changes in translational, rotational, and vibrational energy in a molecule.—In the process of cooling gaseous oxygen from room temperature to near absolute zero,

$$O_2(\text{gas}, 300°\text{K}) = O_2(\text{gas}, 0°\text{K}), \quad (5)$$

the energy given up by the system to the surroundings is about 2×10^3 cal/mole.

Processes involving changes in mechanical potential energy.—When a mass of water is dropped from a height of 555 feet, the energy given up by the system to its surroundings is about 7 cal/mole.

Processes involving changes in mechanical kinetic energy.—In the stopping of a mass of water traveling with a speed of 50 miles per hour, the energy given up by the system to its surroundings is about 1 cal/mole.

In every process that occurs, every change in energy must be in accord with the first law of thermodynamics. This law governs not only the transfer of energy from one place to another, but also all the transformations of energy in its various forms.

The first law of thermodynamics was contained implicitly in the work of Carnot(*1*) in 1824 and of Mayer (*2*) in 1842, but was first stated unambiguously by Helmholtz(*3*) in 1847. The first law may be summed up in the statement that the energy of the universe

remains constant. That is to say, whenever any process occurs, the sum of all the changes in energy, taken over all the systems participating in the process, is zero:

$$\Sigma \, dE = 0. \tag{6}$$

In equation 6, E represents the energy of a given thermodynamic system, and the summation is to cover all systems.

In subjecting a given process to the scrutiny of the first law, it is usually convenient to specify or define a particular system which is inclosed by a surface through which passes, in or out, energy in its various forms, and to let all the other possible systems constitute one large surrounding system. Whenever any process occurs the net energy taken up by the given system will be exactly equal to the energy lost by the surroundings, and vice versa. The increase in the energy, E, of a given system participating in a process will be equal to the sum of all the different kinds of energy taken up by the system from the surroundings less the sum of all the different kinds of energy lost by the system to the surroundings. This may be expressed by the following relation, in which, for later convenience, three kinds of energy are distinguished:

$$dE = \delta q + \delta w + \delta u. \tag{7}$$

In equation 7, dE is the differential increase in the energy of the system, and δq, δw, and δu are infinitesimal quantities of the various kinds of energy taken up by the system, with q representing heat energy, w representing "PV" work energy, and u representing all other forms of energy. In order to be added properly, the energies q, w, and u must be expressed in the same unit of energy, and must be labeled properly with respect to sign. Positive values of q, w, and u indicate that the given energy has been taken up by the system from the surroundings. Correspondingly, negative values of q, w, and u indicate that the given energy has been lost by the system to the surroundings.

Consider a process in which a given system passes from an initial state A to a final state B. During the process, the following amounts and kinds of energy pass into or from the system: a units of heat energy, b units of mechanical potential energy, c units of mechanical kinetic energy, d units of electrical energy, and f units of radiation energy pass from the surroundings into the system; g units of heat energy, h units of mechanical potential energy, i units of mechanical kinetic energy, j units of electrical energy, and k units of radiation energy pass from the system to the surroundings. The increase in the energy of the system as it passes from state A to state B is

$$E_B - E_A = \Delta E = a + b + c + d + f - g - h - i - j - k \tag{8}$$

or, in general, the increase in energy of the system is

$$\Delta E = q + w + u, \tag{9}$$

where q is the algebraic net amount of heat energy, w is the algebraic net amount of "PV" work energy, and u is the algebraic net amount of all other kinds of energy, passing into the system.

If the given process is performed in such a way that the pressure P of the system differs from the resisting pressure on expansion, or the impressed pressure on compression, only by a differential amount, then

$$\delta w = -P dV. \tag{10}$$

For such a case, equation 7 becomes

$$dE = \delta q - P dV + \delta u \tag{11}$$

or

$$dE + P dV = \delta q + \delta u. \tag{12}$$

When the pressure is constant,

$$P dV = d(PV), \tag{13}$$

and equation 12 becomes

$$d(E + PV) = \delta q + \delta u. \tag{14}$$

Further, if for this special case there is no energy involved other than heat energy and "PV" work energy, then

$$\delta u = 0 \tag{15}$$

and equation 14 becomes

$$d(E + PV) = \delta q, \tag{16}$$

which is applicable to a process occurring at constant pressure, with no energy other than heat energy and "PV" work energy. Because the combination of properties, $E + PV$, occurs frequently in thermodynamic problems, it is convenient to let

$$H = E + PV, \tag{17}$$

where H is named the heat content (or enthalpy). Equation 16 then becomes

$$dH = \delta q, \tag{18}$$

which is the relation by which calorimetric measurements of the heat energy associated with a specified reaction or process may be used to evaluate the change in heat content, ΔH, for the given reaction or process.

It is important to note that the first law of thermodynamics is concerned only with changes in the energy of material systems and not with the absolute value of the energy of any system. However, in making thermodynamic calculations of energy, particularly of the energy of chemical reactions, it is convenient to select certain reference states of the substances to which are arbitrarily assigned values of zero energy. Such reference states may be, for example, the chemical elements in the physical state in which they occur naturally at 25°C., or they may be the chemical atoms in the gaseous monatomic state at the absolute zero of temperature, or they may be, also at the absolute zero of temperature, the neutrons, protons, and electrons from which atoms may be formed.

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

Every system, if left to itself, changes rapidly or slowly in such a way as to approach a definite final state of rest or equilibrium(*4*,*5*). Examples of processes tending toward such equilibrium are the following: The diffusion of solute material from a concentrated solution into a dilute solution, leading to uniform concentration; the passage of heat from a hot body to a cold body, leading to uniformity of temperature; the combustion of coal in air; the running down of a mechanical clock.

As these processes tend toward their final state of rest or equilibrium, the systems lose some measure of their capacity for spontaneous change. If we wish to harness one of these spontaneously occurring processes to do useful work, we would select one removed as far as possible from its state of rest or equilibrium, and which has a sufficiently high rate of change toward that equilibrium.

The passage of a system toward equilibrium does not necessarily mean that its energy is decreasing. That energy may be constant. What is being lost is the capacity of the system for spontaneous change.

This brings us to the idea that there exists a property of every thermodynamic system, called its entropy, S, which is associated with its capacity for spontaneous change. The property is characterized by the fact that it is fully conserved over all systems for every reversible process, in which every driving force or pressure differs from the resisting force or pressure only by a differential amount, but increases for all other processes.

Whenever any process occurs, under any conditions, the sum of all the changes in entropy, taken over all the systems involved, is equal to or greater than zero:

$$\Sigma\, dS \geqq 0. \tag{19}$$

When the given process is a reversible one, the sum of all the changes in entropy, taken over all the systems participating in the reversible process, is equal to zero:

$$\Sigma\, dS = 0. \tag{20}$$

In subjecting a given process to the scrutiny of the second law of thermodynamics it is usually convenient to specify or define a particular system, and to let all other possible systems constitute one large surrounding system. Whenever any reversible process occurs, the increase in the entropy of the given system is equal to the decrease in the entropy of the surroundings, and vice versa.

The change in entropy of a given system participating in a reversible process is quantitatively defined as

$$dS = \delta q/T. \tag{21}$$

In equation 21, dS is the differential increase in entropy of the given system and δq is an infinitesimal quantity of heat energy absorbed by the given system at the absolute

temperature T. Equation 21 may also be written as

$$\delta q = T\mathrm{d}S. \qquad (22)$$

When any system passes from an initial state A to a final state B in any given process, the value of the change in entropy is independent of the path or manner of the change, being fixed entirely by the properties of the states A and B. For example, consider the expansion at constant temperature of one mole of an ideal gas from an initial pressure, P_A, and volume, V_A, to a final pressure, P_B, and volume, V_B. The change in entropy for this process is, irrespective of the path,

$$\Delta S = S_B - S_A. \qquad (23)$$

If the expansion occurs freely, with no resisting pressure, no useful work will be produced in the expansion. If the expansion occurs reversibly, with the resisting pressure being always less than the pressure of the gas, P, by an amount $\mathrm{d}P$, a maximum amount of useful work will have been obtained. In either case, the value of the change in entropy is the same.

In general, the change in entropy for any process having known initial and final states can be evaluated as the negative of the process of restoring the system reversibly to its initial state from the final state. In the above example of the isothermal expansion of an ideal gas, the value of $S_B - S_A$, in whatever manner the expansion occurred, could be evaluated as the negative of the change in entropy associated with the isothermal and reversible compression of the ideal gas from state B to state A. The evaluation would involve measurement of the heat given up by the system (one mole of ideal gas) to the surroundings during the isothermal and reversible compression.

EQUILIBRIUM AND FREE ENERGY

Criterion of equilibrium.—For a reversible process, the first law gives the relation (equation 11)

$$\mathrm{d}E = \delta q - P\mathrm{d}V + \delta u, \qquad (24)$$

and the second law gives the relation (equation 22)

$$\delta q = T\mathrm{d}S. \qquad (25)$$

Combination of these equations, with rearrangement of the terms, yields the following important relation applicable to a process performed reversibly:

$$-\delta u = -(\mathrm{d}E + P\mathrm{d}V - T\mathrm{d}S). \qquad (26)$$

This interesting relation tells us that for any process performed reversibly the useful energy obtainable from the system is completely expressible in terms of the five fundamental thermodynamic properties P, V, T, E, and S. That is to say, $-\delta u$ is the useful energy available or the energy which is free to be put to some useful purpose. Whenever $-\delta u$ has a positive value, that is, when the given process gives up some useful energy, it is associated with the spontaneous passage of the system toward its state of rest or equilibrium.

When $-\delta u$ has a negative value (or δu has a positive value), some useful energy must be supplied by the surroundings to the system in order to carry on the specified process. In the latter case, the process is one which cannot proceed spontaneously. In this case, therefore, the given change must be in a direction away from equilibrium, since movements toward equilibrium are ones which occur of their own accord, and those away from equilibrium are ones which do not occur of their own accord.

In the case where

$$\delta u = 0, \qquad (27)$$

no useful energy passes from or into the system in the given process, and it follows that the system is moving neither toward equilibrium (yielding energy, with $-\delta u$ positive) nor away from equilibrium (requiring energy to be supplied, with $-\delta u$ negative). Hence, the system must already be at the state of equilibrium.

Therefore, equation 27, or its equivalent,

$$\delta u = \mathrm{d}E + P\mathrm{d}V - T\mathrm{d}S = 0 \qquad (28)$$

may be used as the general criterion of equilibrium.

Free energy.—Many processes take place at constant pressure and temperature. Under such circumstances,

$$P\mathrm{d}V = \mathrm{d}(PV) \qquad (29)$$

and

$$TdS = d(TS). \quad (30)$$

Combination of equations 28, 29, and 30 yields for the criterion for equilibrium at constant pressure and temperature,

$$d(E + PV - TS) = 0. \quad (31)$$

The combination of properties, $E + PV - TS$, occurs frequently in chemical thermodynamic problems, and it is convenient to let

$$F = E + PV - TS, \quad (32)$$

where F is named the free energy. (At constant pressure and temperature, the decrement in the value of F is the energy which is free to be put to useful purposes.) With this notation, equation 31 becomes

$$dF = 0. \quad (33)$$

That is, at constant pressure and temperature, the criterion for equilibrium is that the change in free energy is zero.

It should be noted that the definitions of the two functions H (equation 17) and F (equation 32) are such as to produce the relation

$$F = H - TS. \quad (34)$$

Free energy of an ideal gas.—When a given system participates in a reversible process in which only heat energy and "PV" work energy occur, then

$$\delta u = 0 \quad (35)$$

and

$$dE + PdV - TdS = 0. \quad (36)$$

Differentiation of the equation defining F yields

$$dF = dE + PdV + VdP - TdS - SdT. \quad (37)$$

Combination of equations 36 and 37 yields

$$dF = VdP - SdT. \quad (38)$$

At constant temperature, equation 38 reduces to

$$dF = VdP, \quad (39)$$

which gives the change of free energy with pressure at constant temperature. Similarly, at constant pressure, equation 38 reduces to

$$dF = -SdT, \quad (40)$$

which gives the change of free energy with temperature at constant pressure.

If the given substance subjected to the foregoing process is an ideal gas, then

$$V = RT/P \quad (41)$$

and equation 39 becomes

$$dF = VdP = (RT/P)dP = RTd\ln P. \quad (42)$$

Equation 42 gives the change of free energy of an ideal gas with pressure at constant temperature.

Equilibrium constant for reactions involving ideal gases.—Let us consider a simple chemical reaction occurring in the ideal gaseous state at a given temperature:

$$mM(gas) = nN(gas). \quad (43)$$

Here, M and N denote the reactant and the product substances respectively and m and n are small integers giving the stoichiometric relation between the number of moles of the two kinds of substances participating in the reaction.

For the substances M and N in certain states s, we may write the change in free energy for this reaction as

$$\Delta F_s = n(F_N)_s - m(F_M)_s. \quad (44)$$

Similarly for the substances M and N in certain states e, we may write the change in free energy as

$$\Delta F_e = n(F_N)_e - m(F_M)_e. \quad (45)$$

Subtraction of equation 45 from equation 44 gives

$$\Delta F_s - \Delta F_e = n(F_s - F_e)_N - m(F_s - F_e)_M \quad (46)$$

which is the difference in the change of free energy for the two sets of conditions.

Integration of equation 42 between the pressure corresponding to the states s and e, respectively, yields, for the difference in free energy of one mole of the ideal gas M between the states s and e

$$(F_s - F_e)_M = RT\ln(P_s/P_e)_M. \quad (47)$$

and similarly for the ideal gas N,

$$(F_s - F_e)_N = RT\ln(P_s/P_e)_N. \quad (48)$$

Combination of equations 46, 47, and 48 yields

$$\Delta F_s - \Delta F_e = nRT\ln(P_s/P_e)_N - mRT\ln(P_s/P_e)_M. \quad (49)$$

Rearrangement of equation 49 gives

$$\Delta F_s - \Delta F_e = RT\ln(P_N^n/P_M^m)_s - RT\ln(P_N^n/P_M^m)_e. \quad (50)$$

Letting

$$Q = P_N^n/P_M^m \quad (51)$$

be the "proper quotient of pressures" for the reaction given in equation 43, we may write equation 50 as

$$\Delta F_s - \Delta F_e = RT\ln Q_s - RT\ln Q_e. \quad (52)$$

Let the states s be identified as standard states, with

$$P_M = P_N = 1. \quad (53)$$

Then

$$Q_s = 1 \text{ and } RT\ln Q_s = 0. \quad (54)$$

Following the nomenclature of Lewis and Randall (*4*) for designating standard states, we write

$$\Delta F_s = \Delta F^\circ. \quad (55)$$

Let the states e be identified as equilibrium states. Then for these states the "proper quotient of pressures" is defined as the equilibrium constant, K,

$$Q_e = K, \quad (56)$$

and, from equation 33, the change in free energy at equilibrium at constant temperature and pressure is zero, so that

$$\Delta F_e = 0. \quad (57)$$

On appropriate substitution into equation 52, one obtains the familiar relation between the equilibrium constant and the standard change in free energy:

$$\Delta F^\circ = -RT\ln K. \quad (58)$$

From equation 34, we may write for any reaction

$$\Delta F = \Delta(H - TS) = \Delta H - \Delta(TS). \quad (59)$$

At constant temperature, this equation becomes

$$\Delta F = \Delta H - T\Delta S. \quad (60)$$

If each reactant and product is in its thermodynamic standard state, then, further,

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K. \quad (61)$$

From this equation, we may write the equilibrium constant explicitly as

$$K = (e^{\Delta S^\circ/R})\,(e^{-\Delta H^\circ/RT}). \quad (62)$$

For any reaction, equation 62 shows that the atoms constituting the molecules involved in the reaction will tend to go preferentially into those molecular configurations in which the entropy is greatest and in which the energy is lowest (algebraically). The greatest entropy is in general associated with those molecular configurations having the largest number of states of existence, that is, those molecular configurations in which the atoms will have the greatest freedom of existence. On the other hand, the lowest energy is in general associated with those molecular configurations in which the atoms are bound most strongly, one to another, that is those molecular configurations in which the atoms will have the greatest structural security. The final state of equilibrium is a compromise between these two opposing tendencies, toward maximum freedom on the one hand and maximum security on the other.

Further examination of equation 62 shows that for those reactions in which the values of ΔS° and ΔH° do not change too greatly with temperature, the equilibrium at low temperatures is determined largely by the value of ΔH°, the "security" term, whereas at high temperatures the equilibrium is determined largely by the value of ΔS°, the "freedom" term.

In considering the possible production of a needed material of commerce by means of a number of proposed chemical reactions, one of the practical things to be known first

about each reaction is the value of the equilibrium constant as a function of temperature. For many reactions it is not possible to determine the equilibrium constant directly, except at a prohibitive cost, and it becomes necessary to evaluate the equilibrium constant by means of the standard change in entropy, $\Delta S°$, and the standard change in heat content, $\Delta H°$, for each reaction.

The values of the standard change in entropy, $\Delta S°$, for a given reaction may be obtained from the values of the entropies of each of the reactants and each of the products. The values of the entropies of the individual compounds may be determined by application of the third law of thermodynamics to measurements of heats of transition, fusion, and vaporization, and heat capacities, down to low temperatures or by statistical calculations utilizing spectroscopic and other molecular data.

The values of the standard change in heat content, $\Delta H°$, may be obtained from calorimetric measurements of the heats of appropriately selected chemical reactions.

From the values of the equilibrium constant as a function of temperature, the optimum temperature of operation for maximum yield is selected. The next point to be investigated is whether, at the selected temperature, the given reaction can be made to proceed at a sufficiently rapid rate for practical operation. Since the rate of reaction increases markedly with temperatures, those reactions to be operated at high temperatures will usually offer little difficulty regarding the rate of reaction, although considerable trouble from the occurrence of undesired side reactions may occur. However, if the reaction is to be run at a low temperature, it will usually be necessary to find for the given reaction a specific catalyst which will produce a sufficiently rapid rate without introducing a significant amount of undesired side reaction.

EVALUATION OF HEATS OF REACTION

The ideal thermochemical table is one which will permit the calculation of the heat of every chemical reaction. Obviously it would be impractical to list in a table the heat of every reaction, but the same end is accomplished by listing for each chemical substance its heat of formation from the elements in selected standard states. It is evident that, by proper selection, the number of chemical reactions whose heats must be measured will be about the same as the number of substances listed in the table. Some saving in the number of reactions to be measured will occur among the organic compounds because of certain correlations which permit the evaluation of the heat of formation of higher members of homologous series, similar isomeric structures, etc.

The value of the heat of formation of a given substance may be the result of the determination of the heat of one reaction, as in the formation of liquid water from gaseous oxygen and hydrogen. For many other substances, however, the value will result from the measurement of the heats of several reactions. For example, the value of the heat of formation of methane, from its elements carbon and hydrogen, depends upon measurements of the heats of the following three reactions: the heat of combustion of gaseous methane in gaseous oxygen to form liquid water and gaseous carbon dioxide; the heat of combustion of solid carbon in gaseous oxygen to form gaseous carbon dioxide; and the heat of combustion of gaseous hydrogen in gaseous oxygen to form liquid water.

There will be certain basic values in the table which will be used very frequently in the derivation of other values. These basic values, which should be known with considerable accuracy, include the heats of formation of water, carbon dioxide, nitric acid, sulfuric acid, hydrogen chloride, hydrogen sulfide, and others. Because of this interdependence of many of the values of heats of formation, it is extremely desirable that values for the important thermochemical constants be carefully selected, and when any change is made in any one of the basic values, corresponding changes should be made in all the values which depend upon it. It is for this same reason that the addition or substraction of values of heats of formation from different thermochemical tables is a precarious undertaking.

In order to determine the value of the heat of formation of a substance, one selects for measurement reactions in which all the

reactants and products, except the given substance, are either elements in their standard reference states or are substances whose heats of formation are known.

The chemical reactions whose heats are to be measured must be ones which proceed to completion (except in so far as a small amount of side reaction is known and can be corrected for) and for which the amount of reaction can be accurately measured.

The principle of the modern experimental method in thermochemistry is to carry out the reaction to be studied in the calorimeter in such a manner that it will be possible to compare the heat evolved by the chemical reaction with the heat evolved by electrical energy or with the heat evolved by a measured amount of a standard chemical reaction, the heat of which has already been compared with electrical energy.

EVALUATION OF ENTROPIES

Entropies from the third law of thermodynamics.—In evaluating entropies by means of the third law of thermodynamics, use is made of the relation (equation 21) given by the second law, namely,

$$dS = \delta q/T. \qquad (63)$$

On integration of this relation, we obtain

$$S - S_0 = \int_0^T \delta q/T, \qquad (64)$$

where S_0 is the entropy of the given system (substance) at the absolute zero of temperature. Actually, of course, measurements can not be carried to the absolute zero of temperature. The investigator makes measurements down to the lowest temperature, T_*, attainable in the given investigation, at which temperature the substance should be in the condensed state, and the values of the integral below T_*, are obtained by extrapolation. Indicating this fact, we may write

$$S - S_0 = \left(\int_0^{T_*} \delta q/T\right)_{\text{extrap.}} + \int_{T_*}^{T} \delta q/T. \qquad (65)$$

The last term on the right side of equation 65 is evaluated completely from the experimental observations of heat capacity, and heats of transition, fusion, and vaporization. The first term on the right side of equation 65 is obtained by extrapolating from T_* to the absolute zero of temperature the measurements of heat capacity made above T_*, in conjunction with an appropriate theoretical equation, usually the Debye (*6*) equation for the heat capacity of solids. The extrapolation from T_* to 0°K in this way accounts for the ordinary thermal entropy resident in the substance at T_*, the lowest temperature of measurement. The term S_0 represents, therefore, the entropy of the substance at the absolute zero of temperature as determined essentially by its quantum condition at T_*.

A simple statement of the third law is the following: "If at the lowest temperature of measurement, T_*, the substance is in a single pure quantum state of energy, except for the ordinary thermal energy characteristic of T_* that is accounted for by the extrapolation from T_* to 0°K, then S_0 may be placed equal to zero." When this condition holds, then equation 65 becomes

$$S = \left(\int_0^{T_*} \delta q/T\right)_{\text{extrap.}} + \int_{T_*}^{T} \delta q/T. \qquad (66)$$

In such cases, the entropy at the temperature T is determined almost completely from the calorimetric observations. (It is obvious that T_* should be made as low as possible in order that the extrapolation shall introduce as small an uncertainty as possible.)

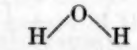
From the data which are now available, it is known that many molecules, including all of the large number of hydrocarbons so far measured, conform to the requirements of the third law as stated above. On the other hand, the following substances have been measured calorimetrically down to the temperature of liquid hydrogen and have, for the reasons indicated, been found to possess at the lowest temperature of measurement, T_*, entropy in excess of that associated with the ordinary thermal energy characteristic of the crystal at T_*: ordinary hydrogen, H_2, and "heavy" hydrogen, H_2^2 or D_2, entropy associated with a non-equilibrium distribution of the molecules among the odd and the even levels of energy (so-called mixture of ortho and para hydrogen) (*7*); ordinary water, H_2O, and "heavy" water, H_2^2O or D_2O, entropy associated with the randomness of arrangement of the hy-

drogen bonds in the crystal (*8*); carbon monoxide, CO, nitric oxide, NO, and nitrous oxide, NNO, entropy associated with a random or partially random "end-for-end" arrangement of the molecules in the crystal (*9, 10, 11, 12*).

[For detailed discussion regarding entropy and the third law of thermodynamics, the reader is referred to Lewis and Randall (*4*), Eastman (*13*), and Pauling and Eastman (*14*).]

Entropies from statistical calculations.— Theoretical and experimental investigations in physics and chemistry have yielded a relatively simple picture of molecular structure which is in substantial accord with all known facts and accepted theories.

For example, consider the water molecule, H_2O, in the gaseous state, at a pressure sufficiently low that interactions between the molecules are negligible. The picture is one of a symmetrical triangular-shaped molecule



with the oxygen atom between, and bonded to, the two hydrogen atoms. The angle formed by the three atoms is 104°27′, and the centers of the hydrogen atoms are 0.9584×10^{-8} cm from the center of the oxygen atom (*15*).

The molecule has a total of nine degrees of ordinary freedom (three times the total number of atoms in the molecule), of which three are translational, three are rotational, and three are vibrational. For simplicity, we may consider that there is a complete set of discrete levels of energy associated with each degree of freedom. (Actually, the situation is considerably simplified for translation because the three degrees of translational freedom are identical and fully "excited" (see later discussion) to their classical values, and is more complicated for rotation and vibration because of interactions between them.) According to the simple picture, a single gaseous water molecule will have at a given instant an amount of energy which is the sum of nine discrete quantities, one from each of the nine sets of levels of energy. Each set of levels of energy may be represented as follows:

Energy levels	Number of the given level	Energy of the given level	Number of states at the given level
———	i	ϵ_i	g_i
	⋮	⋮	⋮
———	3	ϵ_3	g_3
———	2	ϵ_2	g_2
———	1	ϵ_1	g_1
———	0	ϵ_0	g_0

The levels of energy are numbered as indicated, beginning with zero at the bottom, lowest, or ground level. The energy of each level is represented by ϵ_0, ϵ_1, ϵ_2, ϵ_3, $\cdots$ ϵ_i. The multiplicity, or number of individual states existing at each level of energy, is given by g_0, g_1, g_2, g_3, $\cdots$ g_i. The distribution of molecules among the possible levels of energy is given by the Boltzmann distribution law:

$$n_i = n_0 \, e^{-(\epsilon_i - \epsilon_0)/kT}. \qquad (67)$$

This equation gives the population of each state at each level of energy, as a function of the temperature, in terms of the number of molecules in one state at the ground level. The calculation requires only the specification of the temperature and a knowledge of the difference in energy between each possible level and the ground level. Simple application of equation 67 indicates that at the absolute zero of temperatue all the molecules would be on the ground state and that at a temperature which is extremely large (in comparison to the value of $(\epsilon_i - \epsilon_0)/k$) the molecules would be distributed substantially uniformly in number over all the possible states of energy. This latter statement corresponds to having that particular degree of freedom fully "excited" to its classical value. This is so in the case of the three translational degrees of freedom even down to temperatures very near the absolute zero.

At sufficiently high temperatures, we need to consider, in addition to translation, rotation, and vibration, also a new degree of freedom arising from excitation of the valence electrons in the molecule, which gives rise to a set of levels of electronic energy.

The order of magnitude of the spacing of the levels of energy near the ground level in the various sets of energy levels is as

follows, in cal/mole: translational, 10^{-21}; rotational, 10 to 10^2; vibrational, 10^3 to 10^4; electronic, 10^4 to 10^5. We can calculate from equation 67 that for one mole of molecules at room temperature the population of molecules in the first state of electronic energy will usually be entirely negligible, and that the population in the first vibrational state will be very small; whereas, the rotational degrees of freedom will usually be nearly fully "excited" and the translational degrees of freedom will always be fully "excited".

For our calculation, we may take the total number of molecules as one mole, N, approximately 6×10^{23}. Then

$$N = \Sigma n_i g_i = \Sigma n_0 g_i e^{-(\epsilon_i - \epsilon_0)/kT} \quad (68)$$

or, since n_0 is constant at a given temperature,

$$n_0 = N/\Sigma g_i e^{-(\epsilon_i - \epsilon_0)/kT} \quad (69)$$

Combination of equations 67 and 68 gives

$$n_i = N(e^{-(\epsilon_i - \epsilon_0)/kT})/\Sigma g_i e^{-(\epsilon_i - \epsilon_0)/kT}. \quad (70)$$

The total energy of the one mole of molecules, referred to the ground level, is for the given set of energy levels,

$$E\text{-}E_0 = \Sigma n_i g_i(\epsilon_i - \epsilon_0) = N\Sigma g_i(\epsilon_i - \epsilon_0)\,(e^{-(\epsilon_i - \epsilon_0)/kT})/\Sigma g_i e^{-(\epsilon_i - \epsilon_0)/kT}. \quad (71)$$

For convenience, we take the following abbreviations (*16*):

$$A_i = g_i^{-(\epsilon_i - \epsilon_0)/kT} \quad (72)$$

$$B_i = (\epsilon_i - \epsilon_0)A_i \quad (73)$$

$$D_i = (\epsilon_i - \epsilon_0)B_i. \quad (74)$$

It may be noted that

$$dA_i/dT = B_i/kT^2 \quad (75)$$

and

$$dB_i/dT = D_i/kT^2. \quad (76)$$

With these abbreviations, the energy of one mole of molecules at the temperature T, as given by equation 71, is, for the energy from each set of energy levels,

$$E - E_0 = N\Sigma B_i/\Sigma A_i. \quad (77)$$

Once the energy of one mole of molecules is known as a function of the temperature, then the other thermodynamic functions may be evaluated from the ordinary thermodynamic relations. For one mole of molecules in the ideal gaseous standard state (indicated by the superscript °), the following relations hold:

$$PV = RT \quad (78)$$

$$H^\circ = E^\circ + (PV)^\circ = E^\circ + RT. \quad (79)$$

At the absolute zero of temperature (indicated by the subscript $_0$), $T = 0$ and

$$H_0^\circ = E_0^\circ. \quad (80)$$

Then combination of equations 79 and 80 yields the value of the heat content function,

$$(H^\circ - H_0^\circ)/T = (E^\circ - E_0^\circ)/T + R. \quad (81)$$

The heat capacity is given by the relations

$$C_V^\circ = (\delta E^\circ/\delta T)_V \quad (82)$$

or

$$C_V^\circ = (N/kT^2)\,[(\Sigma D_i/\Sigma A_i) - (\Sigma B_i/\Sigma A_i)^2]. \quad (83)$$

The entropy is given by the relation

$$S^\circ = \int C_V^\circ \, d\ln T = \int (\partial E^\circ/\partial T)\, d\ln T \quad (84)$$

or, for each of the sets of energy levels,

$$S^\circ = R\ln \Sigma A_i + (N/T)\,(\Sigma B_i/\Sigma A_i). \quad (85)$$

The free energy function is given by the relation

$$(F^\circ - H_0^\circ)/T = (H^\circ - H_0^\circ)/T - S^\circ \quad (86)$$

or, the contribution from all the sets of energy levels, is

$$(F^\circ - H_0^\circ)/T = R(1 - \ln\Sigma A_i) \quad (87)$$

where Σ indicates that the summation is to be taken over all the different sets of energy levels. It may be noted that, of the

above functions, the free energy function is the most easily calculated since it involves only the terms of ΣA_i. As will be seen later, the free energy function is also one of the most useful for calculations of thermodynamic equilibria.

From the foregoing, it is seen that when the complete diagram of the sets of energy levels is known for a given molecule in the ideal gaseous state, the values of the thermodynamic functions may be calculated accurately in a straightforward manner. The status of the calculation of the contributions to the values of the thermodynamic functions from the several degrees of freedom for a molecule in the ideal gaseous state is as follows (*17*, *18*):

The calculation of the translational contribution may be made accurately for all temperatures for all molecules from the molecular weight, the temperature, and known constants.

The calculation of the rotational contributions may be made quite accurately for all temperatures for the relatively few simple molecules for which a complete diagram of the sets of rotational energy levels is known, and with reasonable accuracy for ordinary and moderate temperatures for those molecules for which the moments of inertia are known (or calculable from the bond angles and distances).

The calculation of the vibrational contributions may be made quite accurately for all temperatures for the relatively few simple molecules for which a complete diagram of the sets of vibrational energy levels is known, and with reasonable accuracy for ordinary and moderate temperatures for those molecules for which the first level is known for each set of levels of vibrational energy. (These are calculable from the fundamental frequencies of vibration.)

The calculation of the electronic contribution, which becomes significant only at relatively high temperatures, can be made only when the appropriate levels of electronic energy are known.

In the case of hydrocarbon and other molecules having groups of atoms which can oscillate with rather large amplitude, or even rotate completely, about a given bond, the determination of the proper set of energy levels to be associated with such a degree of freedom is complicated. When the restriction to rotation is extremely large, the energy levels approach those of a simple harmonic oscillator (for which only the frequency of vibration need be known), while, when the restriction to rotation is extremely small, the energy levels may be taken to be those of a simple rotator (for which only the moment of inertia need be known).

[The reader is referred to Tolman (*17*) and Mayer and Mayer (*18*) for detailed discussions regarding the statistical calculation of thermodynamic functions, and to Pitzer (*19*), Pitzer and Gwinn (*20*), Crawford (*21*), and Wilson (*22*) for detailed discussion of restricted internal rotation as involved in the calculation of thermodynamic functions.]

EVALUATION OF CHEMICAL EQUILIBRIUM CONSTANTS

The increment of the free energy function, $\Delta(F^\circ - H_0^\circ)/T$, for a given reaction is the sum of the values of the free energy function for the products of the reaction less the sum of the values of the free energy function for the reactants:

$$\Delta(F^\circ - H_0^\circ)/T = \Sigma \text{ (products) } (F^\circ - H_0^\circ)/T - \Sigma \text{ (reactants) } (F^\circ - H_0^\circ)/T. \quad (88)$$

But

$$\Delta(F^\circ - H_0^\circ)/T = \Delta F^\circ/T - \Delta H_0^\circ/T. \quad (89)$$

Since, from equation

$$\Delta F^\circ/T = -R\ln K \quad (90)$$

we have

$$R\ln K = -\Delta H_0^\circ/T - \Delta(F^\circ - H_0^\circ)/T. \quad (91)$$

The value of $\Delta H_0^\circ/T$ for any reaction is obtained from the value at 25°C, which is $\Delta H^\circ_{298.16}$, corrected to 0°K by means of the values of the heat content at 298.16°K, referred to 0°K, for the reactants and products:

$$\Delta H_0^\circ = \Delta H^\circ_{298.16} - \Delta(H^\circ_{298.16} - H_0^\circ) \quad (92)$$

where

$$\Delta(H^\circ_{298.16} - H^\circ_0) = \Sigma \text{ (products) } (H^\circ_{298.16} - H^\circ_0) - \Sigma \text{ (reactants) } (H^\circ_{298.16} - H^\circ_0). \quad (93)$$

With the two terms on the right side of equation 91 evaluated as indicated above, the equilibrium constant K can then be evaluated for each of the temperatures of interest.

TABLES OF CHEMICAL THERMODYNAMIC DATA

The calculation of chemical thermodynamic equilibria in chemical reactions is greatly facilitated by the existence of systematic tables giving selected values of the chemical thermodynamic properties of the chemical substances.

The American Petroleum Institute Research Project 44, operating with headquarters at the National Bureau of Standards (under the direction of the writer) and with a unit at the University of California (under the direction of Prof. K. S. Pitzer, at present on leave as director of research of the United States Atomic Energy Commission), is compiling complete tables of the thermodynamic properties of hydrocarbons and related compounds (*23*). To date, this project has issued tables giving values of the following thermodynamic functions:

$(H^\circ - H^\circ_0)/T$, the heat content function
$(F^\circ - H^\circ_0)/T$, the free energy function
S°, the entropy
$H^\circ - H^\circ_0$, the heat content
C_P°, the heat capacity
ΔHf°, the heat of formation from the elements
ΔFf°, the free energy of formation from the elements
$\log_{10} Kf$, the logarithm of the equilibrium constant of formation from the elements.

In the tables cited (*23*), values for the foregoing functions are given as a function of temperature, usually 0° to 1500°K for the hydrocarbons, but to higher temperatures for the nonhydrocarbons, for the following compounds in the gaseous state:

O, H, N, C.
O_2, H_2, OH, H_2O, N_2, NO, CO, CO_2.
Paraffins, C_1 to C_8, all isomers.
Monoolefins, C_2 to C_6, all isomers.
Diolefins, C_3 to C_5, all isomers.
Acetylenes, C_2 to C_5, all isomers.
Alkyl cyclopentanes, C_5 to C_7, all isomers.
Alkyl cyclohexanes, C_6 to C_8, all isomers.
Alkyl benzenes, C_6 to C_9, all isomers.
Styrenes, C_8 and C_9, all isomers.
Cyclopentene and cyclohexene.
Normal paraffins, C_1 to C_{20}.
Normal monoolefins (1-alkenes), C_2 to C_{20}.
Normal acetylenes (1-alkynes), C_2 to C_{20}.
Normal alkyl cyclopentanes, C_5 to C_{21}.
Normal alkyl cyclohexanes, C_6 to C_{22}.
Normal alkyl benzenes, C_6 to C_{22}.

Similar values are also given for solid carbon (graphite).

For most of the above compounds, the same project has also issued tables giving selected values for the following properties:

Heat of formation, free energy of formation, and entropy, for the liquid state at 25°C.
Heat and entropy of fusion
Heat and entropy of vaporization
Standard heat, entropy, and free energy of vaporization, at 25°C.
Heat of combustion, for the gaseous and liquid states, at 25°C.

With the support of the Office of Naval Research of the United States Department of the Navy, the National Bureau of Standards is also compiling tables of selected values of the chemical thermodynamic properties of the chemical substances (*24*). These tables list substantially the same thermodynamic properties and functions given above but cover all of the chemical substances for which thermodynamic data are available. These tables are being issued in three series, as follows:

SERIES I: Heat of formation, free energy of formation, logarithm of the equilibrium constant of formation, entropy, and heat capacity, each at 25°C, for solid, liquid, and gaseous states, as appropriate and known. Also, where calculable, the heat of formation of 0°K.

SERIES II: Heat, temperature, and entropy of transition, fusion, and vaporization, including values of pressure as appropriate and known.

SERIES III: Heat of formation, free energy of formation, logarithm of the equilibrium constant of formation, free energy function, heat content

(or enthalpy) function, entropy, heat content (or enthalpy), and heat capacity, from 0° to high temperatures (in some cases to 5000°K).

The substances listed in the tables are arranged in a manner similar to that used by Bichowsky and Rossini (*25*), with some modification. The chemical elements are arranged in the order shown in Fig. 1. If the elements are taken to be arranged in the order a, b, c, d, e, etc., the chemical substances are in the order: a, b, ba; c, ca, cb, cba; d, da, db, dba, dc, dca, dcb, dcba; etc.

To date, a total of 433 pages of material on selected values of chemical thermodynamic properties has been issued in this work (*24*), including 203 in Series I, 136 in Series II, 79 in Series III, and 15 of constants, conversion factors, and explanatory material. Systematic coverage for Series I and Series II has been completed through the compounds of the mercury group.

EXAMPLES OF CHEMICAL EQUILIBRIA[2]

From the tables of chemical thermodynamic properties mentioned in the preceding section, we can calculate readily the equilibrium constants as a function of temperature for many processes which are important in in the petroleum, chemical, and rubber industries. When the tables give values of $\log_{10}Kf$, the logarithm of the equilibrium constant of formation, for each of the reactants and products of the given reaction, the values of log K for the reaction may be readily calculated for each temperature of interest, as follows: Given a reaction in which b moles of B react with c moles of C to form m moles of M and n moles of N, as

$$bB + cC = mM + nN. \qquad (94)$$

Then, for this reaction,

$$\log_{10}K = \Sigma\,(\text{products})\log_{10}Kf - \Sigma\,(\text{reactants})\log_{10}Kf \qquad (95)$$

or

$$\log_{10}K = (m\log_{10}Kf_M + n\log_{10}Kf_N) - (b\log_{10}Kf_B + c\log_{10}Kf_C). \qquad (96)$$

The values of log K for a given reaction are then plotted against the temperature in order to ascertain the optimum range of temperature for carrying on the given reaction. Positive values of log K for a given reaction indicate higher concentrations for the products of the reaction at equilibrium. Negative values of log K indicate higher concentrations for the reactants at equilib-

[2] Description of the commercial processes mentioned in this section may be found in numerous articles appearing within the past five years in the following journals: Oil and Gas Journal, Petroleum Refiner, and Petroleum Engineer.

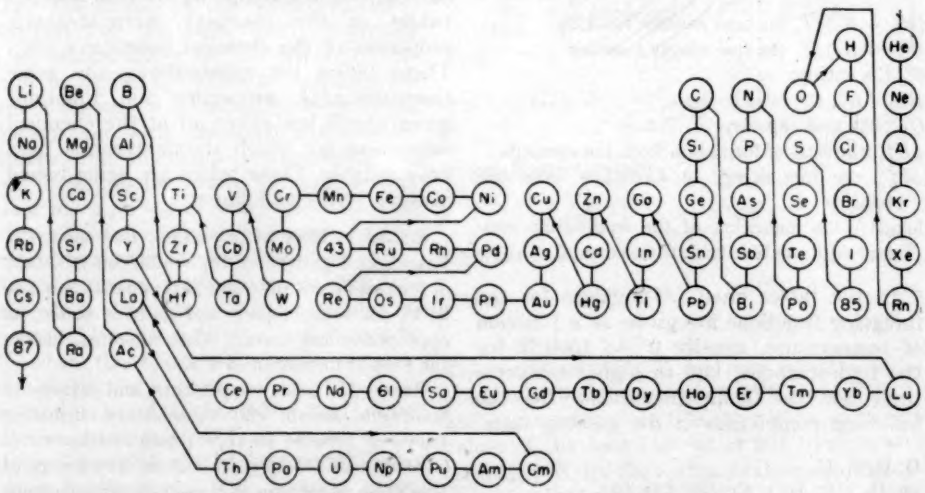


FIG. 1.—Standard order of arrangement of chemical elements.

rium. Hence, large positive values of log K are required for a reaction to proceed as written.

Toluene for explosives.—During the recent war, the requirements for toluene for use in the manufacture of explosives were far beyond all that could conceivably be produced by the conventional method of recovery from coal tar. The petroleum industry quickly brought two new processes into commercial use, both utilizing petroleum stock and achieving a production greatly in excess of that possible from all the coal tar available.

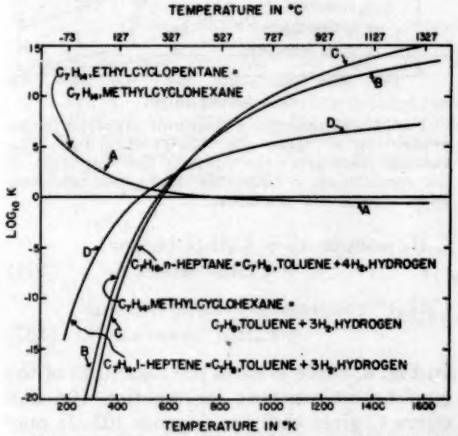


FIG. 2.—Equilibria in reactions involved in the production of toluene from petroleum. The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase.

In one of the new methods, advantage was taken of the fact that the light gasoline fraction of petroleum contains appreciable amounts of toluene, of methylcyclohexane which can be dehydrogenated to toluene, and of ethylcyclopentane and dimethylcyclopentanes which can be isomerized to methylcyclohexane which can then be dehydrogenated to toluene. All the toluene (including that originally present plus the additional amount formed) is then removed from the other hydrocarbons in the original stock by well established methods of extraction, or azeotropic distillation, or extractive distillation. The reactions involved, are as follows, in the sequence of actual operation:

$$C_7H_{14}\text{ (ethylcyclopentane)} = C_7H_{14}\text{ (methylcyclohexane)} \quad (97)$$

$$C_7H_{14}\text{ (methylcyclohexane)} = C_7H_8\text{(toluene)} + 3H_2\text{(hydrogen)}. \quad (98)$$

Curves A and B in Fig. 2 give the logarithm of the equilibrium constant as a function of temperature for reactions 97 and 98, respectively. Curve A shows that the reaction of isomerization is required to be carried out at low temperatures. Curve B shows that the reaction of dehydrogenation of methylcyclohexane to toluene is required to be performed at higher temperatures. In each case, of course, a suitable catalyst is required.

In the second method for producing toluene from petroleum stock, advantage was taken of the fact that, of the several types of hydrocarbons present in the gasoline fraction of petroleum, the aromatic hydrocarbons (benzene, toluene, xylenes, etc.) are the most stable at high temperatures. The operation here is to pass the mixture of hydrocarbons (paraffins, cycloparaffins, olefins, and aromatics) through a catalytic reaction zone at high temperatures in the presence of hydrogen gas. The several general reactions involve the conversion to aromatics of cycloparaffins, paraffins, and olefins, in accordance with the following representative reactions:

$$C_7H_{14}\text{(methylcyclohexane)} = C_7H_8\text{(toluene)} + 3H_2\text{(hydrogen)} \quad (99)$$

$$C_7H_{16}\text{(n-heptane)} = C_7H_8\text{(toluene)} + 4H_2\text{(hydrogen)} \quad (100)$$

$$C_7H_{14}\text{(1-heptene)} = C_7H_8\text{(toluene)} + 3H_2\text{(hydrogen)}. \quad (101)$$

For each of these reactions, a plot of log K vs T is given in Fig. 2. It may be noted that for each of these reactions in the gas phase the equilibrium is most favorable at high temperatures for the production of toluene. One of the practical problems in such high temperature operations is to reduce the amount of side reactions, particularly decomposition to carbon in the form of coke.

"Isooctane" for aviation fuel.—The mili-

tary need for enormous quantities of "high octane" aviation fuel during the recent war was met in appreciable part by the production of "alkylate" and of "hydrocodimer" materials. These materials were blended with regular aviation fuel base stock to give larger quantities of material of sufficiently high quality when appropriately fortified with tetraethyl lead. The production of these materials, which are largely mixtures of branched-chain octanes, was made possible by the discovery of commercially usable catalysts (sulfuric acid and hydrofluoric acid) which were able to make hydrocarbons, previously considered quite inert, react rapidly at room temperature.

"Alkylate" material is the product obtained when isobutane is added to a mixture of butenes (preferably rich in isobutene) to form a mixture of branched-chain paraffins, largely octanes, but containing appreciable amounts of hexanes, heptanes, and lower-boiling nonanes (*26*). Usually the isobutene is obtained from the gases produced as a byproduct of the cracking process. The amount of isobutane available in natural gasoline is augmented by the isomerization of the larger amount of normal butane present in the natural gasoline. The reactions may be represented as follows:

$$C_4H_{10}(\text{normal butane}) = C_4H_{10}(\text{isobutane}) \quad (102)$$

$$C_4H_{10}(\text{isobutane}) + C_4H_8(\text{isobutene}) = C_8H_{18}(\text{"isooctane"}). \quad (103)$$

The logarithm of the equilibrium constant of these reactions are given as curves A and B, respectively, in Fig. 3. The importance of a suitable catalyst is readily seen from the fact that these reactions must be carried out near room temperature in order to have a favorable equilibrium.

"Hydrocodimer" material is the product obtained on the hydrogenation of codimers of the butenes. The product is similar to "alkylate" in consisting largely of branched-chain octanes, and containing also branched-chain hexanes, heptanes, and lower-boiling nonanes, but differs in the relative amounts of the main components (*26*). The two reactions may be represented, in principle, as follows:

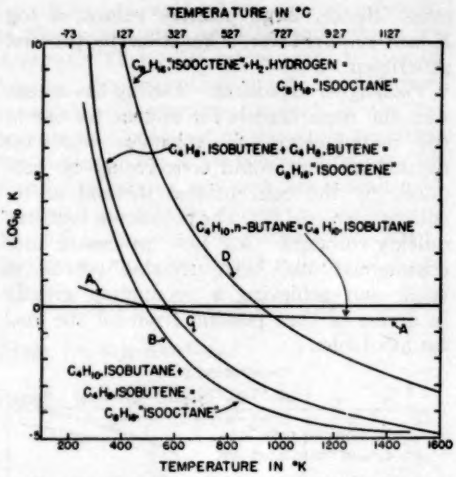


FIG. 3.—Equilibria in reactions involved in the production of "isooctane" for aviation fuel. The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase.

$$C_4H_8(\text{isobutene}) + C_4H_8(\text{1-butene}) = C_8H_{16}(\text{"isooctene"}) \quad (104)$$

$$C_8H_{16}(\text{"isooctene"}) + H_2(\text{hydrogen}) = C_8H_{18}(\text{"isooctane"}). \quad (105)$$

In Fig. 3, curve B gives the logarithm of the equilibrium constant for reaction 104 and curve C gives that for reaction 105. It may be seen that for both reactions the equilibrium is more favorable at low temperatures.

Butadiene and styrene for synthetic rubber.—One of the most remarkable technological accomplishments in history was the creation in this country during the recent war of a synthetic rubber industry, which was necessitated by the stoppage of the supply of natural rubber. The production of regular synthetic rubber today is largely from petroleum stock through the copolymerization of 1,3-butadiene and styrene.

The 1,3-butadiene is made by the dehydrogenation of butenes obtained from the cracking processes, and the reaction may be represented as follows:

$$C_4H_8(\text{1-butene}) = C_4H_6(\text{1,3-butadiene}) + H_2(\text{hydrogen}). \quad (106)$$

Curve A in Fig. 4 gives the logarithm of the

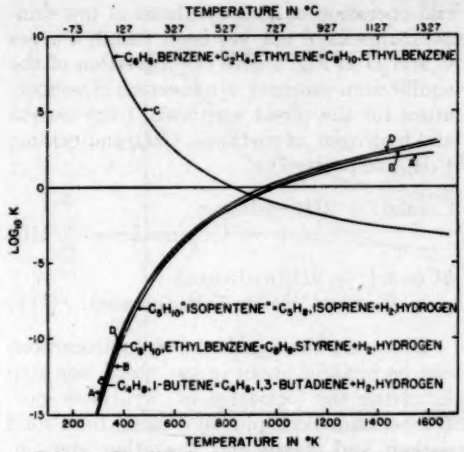


FIG. 4.—Equilibria in reactions involved in the production of components for synthetic rubber. The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase.

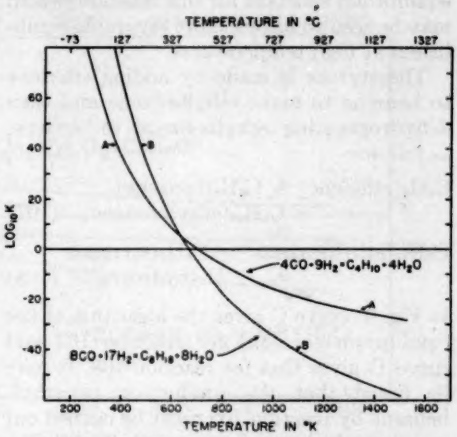


FIG. 6.—Equilibria in reactions involved in the production of synthetic fuels. The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase.

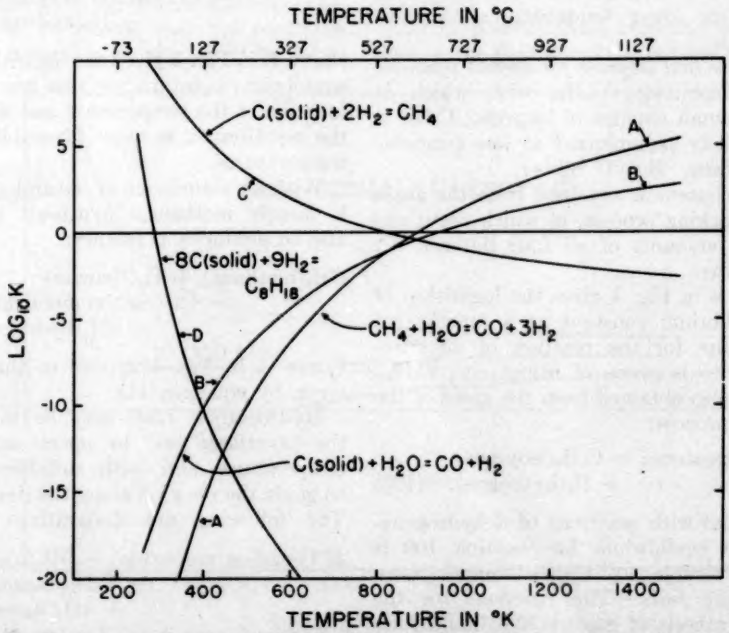


FIG. 5.—Equilibria in reactions involved in the direct synthesis of hydrocarbons and in the production of "synthesis gas" (carbon monoxide plus hydrogen). The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase except for the solid carbon.

equilibrium constant for this reaction, which may be seen to have a more favorable equilibrium at high temperatures.

The styrene is made by adding ethylene to benzene to make ethylbenzene and then dehydrogenating ethylbenzene to styrene, as follows:

$$C_2H_4(\text{ethylene}) + C_6H_6(\text{benzene}) = C_8H_{10}(\text{ethylbenzene}) \quad (107)$$

$$C_8H_{10}(\text{ethylbenzene}) = C_8H_8(\text{styrene}) + H_2(\text{hydrogen}). \quad (108)$$

In Fig. 4, curve C gives the logarithm of the equilibrium constant for reaction 107 and curve D gives that for reaction 108. It may be noted that the production of ethylbenzene by reaction 105 must be carried out at relatively low temperatures whereas the dehydrogenation of ethylbenzene to styrene must be carried out at higher temperatures

The copolymerization of 1,3-butadiene and styrene to form "regular" synthetic rubber is performed near room temperature, with newer developments indicating a better product for lower temperatures of polymerization.

Isobutene and isoprene for special synthetic rubber.—Isobutene, C_4H_8, with which is mixed a small amount of isoprene, C_5H_8, is commercially polymerized at low temperatures to form "Butyl" rubber.

The isobutene is obtained from the gases of the cracking process, in which occur appreciable amounts of all four butenes (C_4 monoolefins).

Curve B in Fig. 4 gives the logarithm of the equilibrium constant as a function of temperature for the reaction of dehydrogenation to isoprene of isopentene, C_5H_{10}, which is also obtained from the gases of the cracking process:

$$C_5H_{10}(\text{isopentene}) = C_5H_8(\text{isoprene}) + H_2(\text{hydrogen}). \quad (109)$$

As is usual with reactions of dehydrogenation, the equilibrium for reaction 109 is more favorable at higher temperatures.

Synthetic fuels.—The reactions for the direct synthesis of gaseous and liquid fuels from carbon and hydrogen have equilibria which are more favorable at low temperatures and suitable catalysts for the commercial operation of such synthesis at low temperatures have not yet been found. Curves C and D in Fig. 5 give the logarithm of the equilibrium constant as a function of temperature for the direct synthesis, from carbon and hydrogen, of methane, CH_4, and octane, C_8H_{18}, respectively:

$$C(\text{solid}) + 2H_2(\text{hydrogen}) = CH_4(\text{methane}) \quad (110)$$

$$8C(\text{solid}) + 9H_2(\text{hydrogen}) = C_8H_{18}(\text{octane}). \quad (111)$$

However, the synthesis of hydrocarbons can be brought about in two steps, one step involving the formation of "synthesis gas" (carbon monoxide plus hydrogen) from solid carbon and steam and the other step involving the reaction of carbon monoxide and hydrogen to form the hydrocarbon and steam. The formation of the "synthesis gas" may be illustrated by the following reaction:

$$C(\text{solid}) + H_2O(\text{steam}) = CO(\text{carbon monoxide}) + H_2(\text{hydrogen}). \quad (112)$$

Curve B in Fig. 5 gives the logarithm of the equilibrium constant for this reaction as a function of the temperature and shows that the equilibrium is more favorable at high temperatures.

With an abundance of natural gas, which is largely methane, "synthesis gas" may also be produced as follows:

$$CH_4(\text{methane}) + H_2O(\text{steam}) = CO(\text{carbon monoxide}) + 3H_2(\text{hydrogen}). \quad (113)$$

Curve A in Fig. 5 applies to the reaction given by equation 113.

Hydrocarbon fuels may be made from the "synthesis gas" by operation at lower temperatures and with suitable catalysts to guide the reaction along the desired path. The following are illustrative reactions:

$$4CO(\text{carbon monoxide}) + 9H_2(\text{hydrogen}) = C_4H_{10}(\text{butane}) + 4H_2O(\text{steam}) \quad (114)$$

$$8CO(\text{carbon monoxide}) + 17H_2(\text{hydrogen}) = C_8H_{18}(\text{octane}) + 8H_2O(\text{steam}). \quad (115)$$

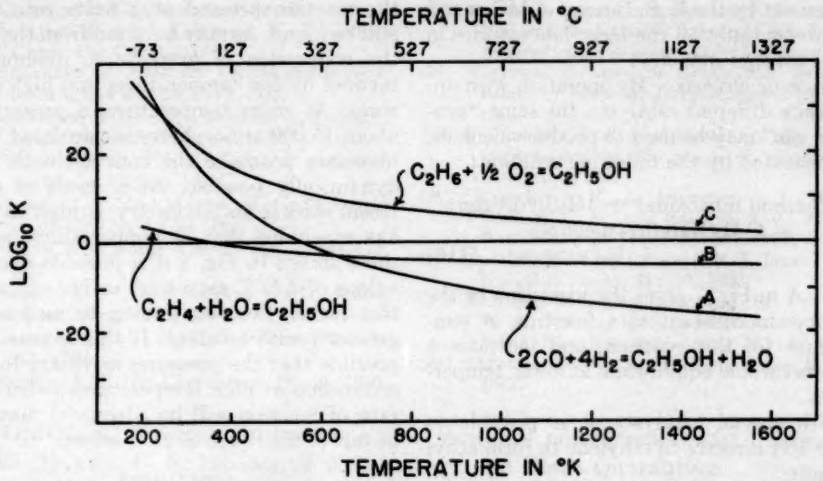


FIG. 7.—Equilibria in reactions involved in the production of synthetic alcohols. The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase.

Curves A and B in Fig. 6 give the logarithm of the equilibrium constant as a function of the temperature for reactions 114 and 115, respectively. It is seen that the equilibria are more favorable at the lower temperatures for these reactions, which are commonly referred to as "Fischer-Tropsch" reactions.

At the present time, extensive investigations in the field of synthetic fuels are being

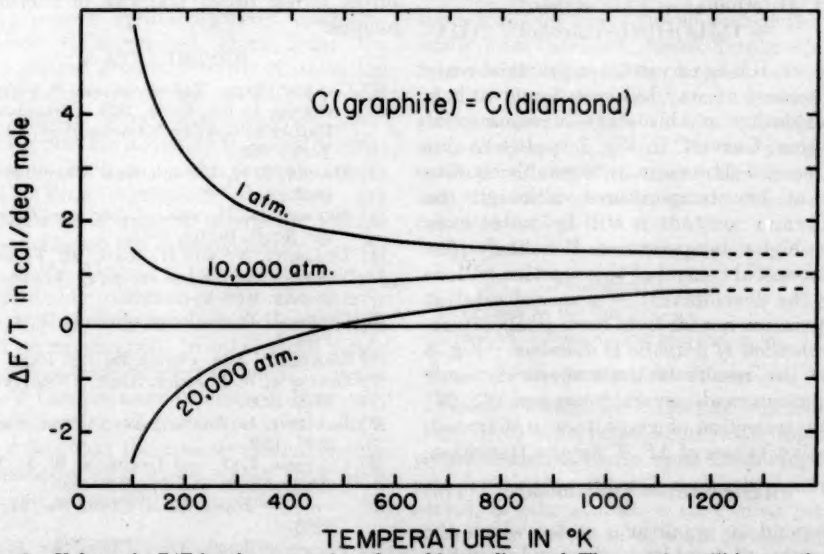


FIG. 8.—Values of $\Delta F/T$ for the conversion of graphite to diamond. The reaction will have a thermodynamic tendency to proceed as written when the value of $\Delta F/T$ is negative. The three curves apply to pressure of 1, 10,000, and 20,000 atmospheres, respectively.

carried out by the U. S. Bureau of Mines and by substantially all the large laboratories in the petroleum industry.

Synthetic alcohols.—By operation with appropriate different catalysts, the same "synthesis gas" may be used to produce alcohols, as illustrated by the following reaction:

$$2CO(\text{carbon monoxide}) + 4H_2(\text{hydrogen}) = C_2H_5OH(\text{ethyl alcohol}) + H_2O(\text{steam}). \quad (116)$$

Curve A in Fig. 7 gives the logarithm of the equilibrium constant as a function of temperature for this reaction, and indicates a more favorable equilibrium at lower temperatures.

With special catalysts, it is possible to add water directly to ethylene to form ethyl alcohol:

$$C_2H_4(\text{ethylene}) + H_2O(\text{steam}) = C_2H_5OH(\text{ethyl alcohol}). \quad (117)$$

Curve B in Fig. 7 applies to this reaction and shows a favorable equilibrium at lower temperatures.

Theoretically, ethane may be oxidized directly to form ethyl alcohol:

$$C_2H_6(\text{ethane}) + \tfrac{1}{2}\,O_2(\text{oxygen}) = C_2H_5OH(\text{ethyl alcohol}). \quad (118)$$

However, this is as yet not a practical reaction because no way has been found to halt the oxidation at this stage in commercial operation. Curve C in Fig. 7 applies to this reaction and shows a more favorable equilibrium at low temperatures, although the equilibrium constant is still favorable even at the higher temperatures. It is likely that the successful control of this reaction will require the development of a special catalyst for operation not far from room temperature.

Transition of graphite to diamond.—Fig. 8 shows the results of some thermodynamic calculations made several years ago (*27*, *28*) on the transition of graphite into diamond. Negative values of $\Delta F/T$ for the transition,

$$C(\text{graphite}) = C(\text{diamond}), \quad (119)$$

correspond to conditions under which the conversion of graphite to diamond would be thermodynamically possible. Of course, for such conditions, a suitable catalyst to make the reaction proceed at a finite rate must still be found. As may be noted from the plot, the conversion of graphite to diamond is favored by low temperatures and high pressures. At room temperature, a pressure of about 15,000 atmospheres is calculated to be necessary to make the conversion thermodynamically possible. As a result of some recent work in his laboratory, Bridgman (*29*) has concluded that at temperatures beyond those shown in Fig. 8 it is possible that the values of $\Delta F/T$ may tend to become negative rather than continuing to increase to greater positive values. If this is true, it is possible that the pressures necessary for the conversion at high temperatures (where the rate of reaction will be adequate) may not be out of the range of attainment.

CONCLUSION

In concluding this discourse on chemical thermodynamics, I would like to recall some words written nearly 30 years ago by Gilbert N. Lewis (*4*) "The fascination of a growing science lies in the work of the pioneers at the very borderland of the unknown, but to reach this frontier, one must pass over well-traveled roads; of these, one of the safest and surest is the broad highway of thermodynamics."

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ENTOMOLOGY.—*Pomerantziidae, a new family of prostigmatic mites.*[1] EDWARD W. BAKER, U. S. Bureau of Entomology and Plant Quarantine.

Upon routine examination of mites collected by W. F. Turner in the course of a survey of the insects in peach orchards in Southern United States, a series of seven specimens was put aside labeled as Stigmaeidae. Recently, while reviewing this family in search of material for a study of the Raphignathidae-Stigmaeidae-Caligonellidae complex, the author noted that these mites possessed genital suckers, which immediately differentiated them from the known related groups. Further examination showed differences in the tarsal claws and tarsal sensory setae, which provide additional support for assigning these mites separate family rank under the present classification. Other variations described are considered as of generic or specific status.

In some cases the existing family classification of the Acarina is based on characters that probably do not justify the family status, and some groups treated as families should be recombined. In other cases single species show such decided systematic breaks that new families must be created. However, the classification of the mites is in such a state of flux that the present system should be considered as a guide rather than as a sound and permanent arrangement.

Pomerantziidae, n. fam.

With palpal thumb-claw complex; mo able chelae short, styletlike; peritreme short, not reaching to inner base of chelicerae; several dorsal shields; no eyes; no differentiated sensory setae; anus terminal; three pairs of genital suckers; seven rodlike and one conelike sensory setae on tarsus I; two rodlike sensory setae on tarsus II; tarsi with claws, without pulvilli.

The presence of the three pairs of genital suckers, the large number of sensory setae on tarsus I, and the lack of pulvilli separate this new family from the closely related Raphignathidae-Stigmaeidae-Caligonellidae complex as well as from the Pseudocheylidae, none of which has genital suckers and in all of which there is only one sensory seta on tarsus I. The first group possesses a pulvillus with tenent hairs while the tarsi of the Pseudocheylidae are variously arranged but not as above.

Type genus.—Pomerantzia, n. g.

Pomerantzia, n. g.

Diagnosis as for the family.

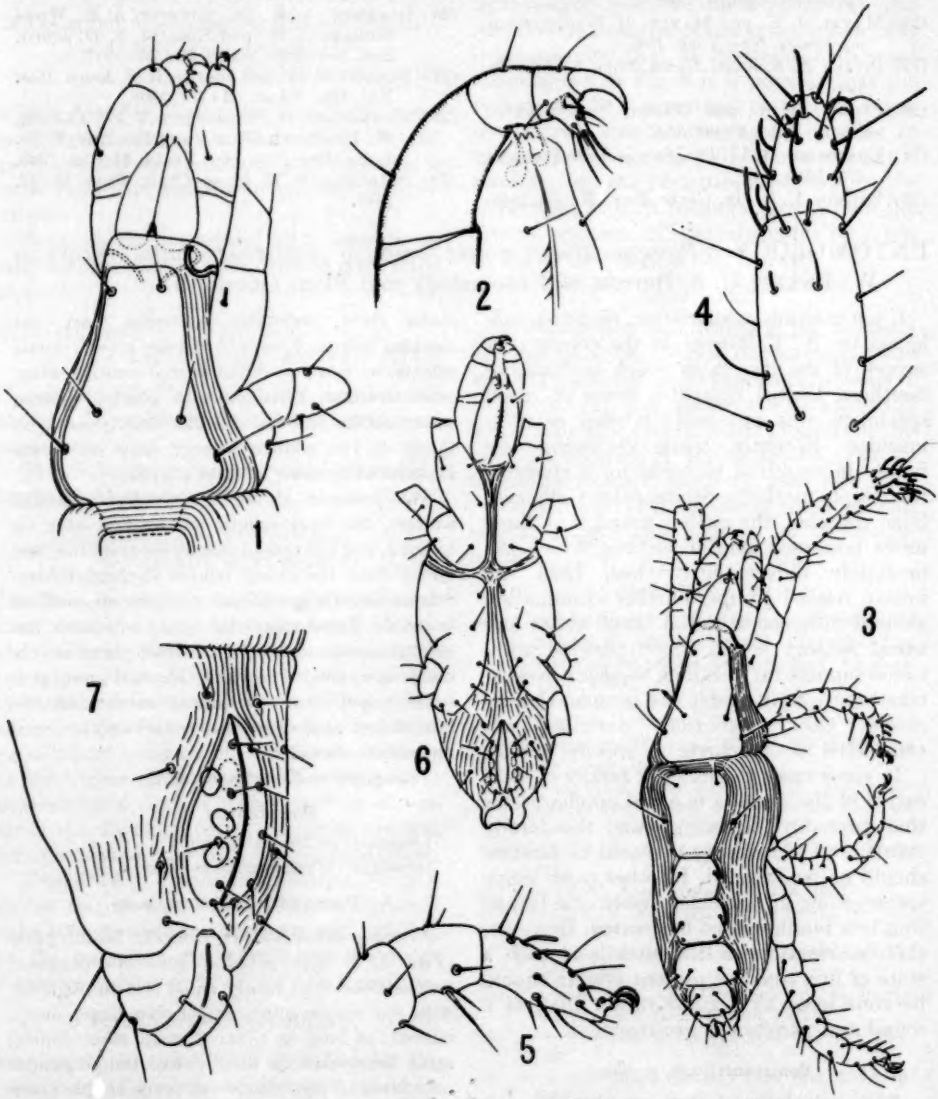
Genotype.—Pomerantzia charlesi, n. sp.

Pomerantzia charlesi, n. sp.

Female.—Small, narrow, elongate. Mouth parts (Figs. 1, 2) with palpal thumb-claw complex; palpus slender, of nearly equal size throughout, with few simple setae; palpal claw large, sharp, curved, as long as tibia; a small stout conical spine below claw on tibia; palpal thumb slender narrowing to tip, with about seven simple distal setae; chelicerae fused basally but suture distinct; movable chela short, styletlike, curved, for pierc-

[1] Received March 25, 1949.

ing, typical for the group; at inner posterior corner of cheliceral bases three pairs of small beadlike segments which could be remnants of peritremes; peritremes (Fig. 1) short, on lateral anterior margins of propodosoma, not reaching to inner posterior margin of chelicerae. Single shield on propodosoma, narrowing anteriorly, surrounded by striated skin, with three pairs of setae, none of which appears to be differentiated into sensory setae. No eyes. Dorsum of hysterosoma (Fig. 3) with five small shields, arranged longitudinally; the first three shields each with a single pair of short setae, the posterior two shields each with two pairs of short setae; the third



FIGS. 1–7.—*Pomerantzia charlesi*, n. sp.: 1, Anterior dorsal portion showing rostrum, propodosoma, and peritreme; 2, palpus; 3, dorsum; 4, tarsus and tibia I; 5, tarsus and tibia II; 6, venter; 7, detail of genital region.

shield with a pair of posterior marginal pores; shields surrounded by striated skin. Anus terminal. Legs stout, with short setae as figured; tarsi with claws, without pulvilli; tarsus I (Fig. 4) with seven rodlike sensory setae and one short conelike spine; tibia I with three rodlike sensory setae; tarsus II (Fig. 5) with two rodlike sensory setae. Coxae arranged in four groups of two each (Fig. 6), separated by striated skin; coxal plates merging as figured to form a more or less ventral armor; coxa I with a short dorsal rodlike seta. Genitalia (Fig. 7) with three pairs of genital suckers; with five pairs of short setae; venter of mite surrounding genital opening striated, with four pairs of setae. Length including rostrum 340μ; width 100μ.

Types.—Type female, U.S.N.M. no. 1858, and five paratypes, all deposited in the U. S. National Museum.

Type habitat.—In peach orchard soil, Upson County, Ga., collected by W. F. Turner, July 3 and 4, 1936.

This mite is named for Charles Pomerantz, of New York City, in recognition of his enthusiastic services to the study of the rickettsial pox disease, which is carried to man by *Allodermanyssus sanguineus* (Hirst), a mite parasite of mice.

ZOOLOGY.—*Some littoral sea-urchins from the Philippines.*[1] AUSTIN H. CLARK, U. S. National Museum.

The American Museum of Natural History, New York, through John C. Armstrong, has recently sent me for examination a collection of littoral sea-urchins made by Dr. Willard G. Van Name and associates in the Gulf of Dávao, southeastern Mindanao, in 1936 and 1937. I much appreciate the courtesy of the American Museum and of Mr. Armstrong in permitting me to study this interesting collection.

Many species of sea-urchins have been recorded from the littoral of the Philippines, but in very few cases are the records accompanied by definite localities or other data.

In 1928 Dr. Hilario A. Roxas published a list of the littoral species contained in the collection of the Department of Zoology, University of the Philippines. His list included 17 species, but two of these, *Echinometra picta* and *E. oblonga*, are synonyms of *E. mathaei*, the commonest species in the islands. His *Prionocidaris baculosa* is, as has been shown by Mortensen, *Eucidaris metularia*, and his *Toxopneustes chlorocanthus* is *T. pileolus*.

The present list includes only 13 species, but 5 of these are not given in Dr. Roxas's list. These are: *Phyllacanthus imperialis*, *Echinothrix diadema*, *Echinostrephus aciculatus*, *Echinodiscus tenuissimus*, and *Echinoneus cyclostomus*.

[1] Published by permission of the Secretary of the Smithsonian Institution. Received March 15, 1949.

Most of Dr. Roxas's specimens came from Puerto Galera, Mindoro. He does not mention any from Mindanao.

CIDARIDAE

Phyllacanthus imperialis (Lamarck)

Locality.—Padada Beach; G. R. Oesch (1 specimen).

Notes.—This is a small specimen 15 mm in diameter with the longest spines 22 mm long. The spines are stoutest in their outer two-thirds. They have two narrow white bands separated by about their own width near the tip. The color is purple.

Plococidaris verticillata (Lamarck)

Localities.—Padada Beach; G. R. Oesch, June 28 to July 8, 1936 (2 specimens and 1 very small broken specimen).

Reef about 1 kilometer north of Digos, Gulf of Dávao; E. H. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

Eucidaris metularia (Lamarck)

Locality.—Padada Beach; G. R. Oesch, July 6 to 19, 1936 (2 specimens).

Padada Beach; G. R. Oesch, March 8, 1936 (1 specimen).

DIADEMATIDAE

Diadema setosum (Leske)

Locality.—Padada Beach; G. R. Oesch (1 specimen).

Notes.—The test is 15 mm in diameter and

the spines are about 38 mm long. The color is dull red, the spines banded with white. The pedicellariae are typical of this species.

Echinothrix diadema (Linné)

Locality.—Reef off Digos, Gulf of Dávao; Ernest H. and G. R. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

Echinothrix calamaris (Pallas)

Locality.—Reef about 1 kilometer north of Digos, Gulf of Dávao; E. H. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

TEMNOPLEURIDAE

Mespilia globulus (Linné)

Locality.—Padada Beach; G. R. Oesch, May 2, 3, July 6 to 19, 1936 (3 specimens).

ECHINOMETRIDAE

Echinostrephus aciculatus A. Agassiz

Locality.—Reef off Digos, Gulf of Dávao; Ernest H. and G. R. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

Echinometra mathaei (de Blainville)

Localities.—Padada Beach; G. R. Oesch, March 8, 14, 16, 19, April 5, 12, May 9, 10, June 5, 6, 20, 21, 25, 26, 28, July 6 to 19, 1936 (91 specimens).

Reef off Digos, Gulf of Dávao; Ernest H. and G. R. Oesch and Dr. W. G. Van Name, November 1937 (4 specimens).

Flats about 1½ miles south of the mouth of the Padada River, Gulf of Dávao; E. H. Oesch and Dr. W. G. Van Name, November 1937 (6 specimens).

Note.—All the specimens from Padada Beach are small.

Heterocentrotus mammillatus (Linné)

Localities.—Padada Beach: G. R. Oesch, June 28 to July 19, 1936 (2 specimens).

One kilometer north of Santa Cruz, Gulf of Dávao; Dr. W. G. Van Name and Felix Barto, November 1937 (4 specimens).

Flats about 1½ miles south of the mouth of the Padada River, near Mangrove Island; E. H. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

Reef off Digos, Gulf of Dávao; Ernest H. and G. R. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

Notes.—In the specimens from Padada Beach the general color was deep red with lighter bands on the spines, and the secondary spines on the abactinal surface whitish.

A large specimen from north of Santa Cruz was very deep red with lighter red bands on the longer spines; the short secondary spines were not very light colored. A smaller specimen from the same locality was browner and in general lighter colored; the short secondary spines were almost white.

LAGANIDAE

Laganum laganum (Leske)

Localities.—Padada Beach; G. R. Oesch, April 5, 12, May 2, 3, 1936 (52 specimens).

Two kilometers north of Digos, Santa Cruz, Gulf of Dávao; E. H. and G. R. Oesch and Dr. W. G. Van Name, November 1937 (24 specimens).

SCUTELLIDAE

Echinodiscus tenuissimus (L. Agassiz and Desor)

Locality.—Two kilometers north of Digos, Santa Cruz, Gulf of Dávao; E. H. and G. R. Oesch and Dr. W. G. Van Name, November 1937 (1 specimen).

ECHINONEIDAE

Echinoneus cyclostomus (Leske)

Locality.—Not given.

Notes.—This is a large specimen 30 mm. long, 26 mm broad, and 16 mm high.

REFERENCE

ROXAS, HILARIO A. *Philippine littoral Echinoida.* Philippine Journ. Sci. **36** (2): 243–270, pls. 1–7 June 1928.

ORNITHOLOGY.—*Races of* Pycnonotus cafer (*Linnaeus*) *and* P. aurigaster (*Vieillot*) *in the Indo-Chinese Subregion.*[1] H. G. DEIGNAN, U. S. National Museum.

Through the courtesy of the authorities of the Museum of Comparative Zoology (M.C.Z.), the American Museum of Natural History (A.M.N.H.), the Academy of Natural Sciences of Philadelphia (A.N.S.P.), and the Chicago Natural History Museum (C.N.H.M.), I have added to the series in the United States National Museum (U.S. N.M.) to make a total of 236 Indo-Chinese specimens of the bulbuls combined by Stuart Baker (Fauna of British India, Birds, ed. 2, **7:** 79–80. 1930) into the "species" *Pycnonotus* (*"Molpastes"*) *cafer* (Linnaeus).

Baker (*ibid.* **1:** 381–382. 1922) has discussed at some length the problem of overlapping brown-eared forms (*cafer*) and white eared forms (*aurigaster*) in these words:

> The question of the status of the Chinese birds *chrysorrhoides* [= *aurigaster*] is one of some doubt. Robinson and Kloss consider that there are two good species, *chrysorrhoides* [= *aurigaster*] and *haemorrhous* [= *cafer*], both containing one or more races. To me it seems that we have but one species, extending from Ceylon to China, for there is no real break in the continuity of gradation from the dark western forms with black ear-coverts to the pale eastern forms with almost white ear-coverts. At the same time, all along the joining line of *Molpastes h. burmanicus*, *M. h. nigripileus* and *M. h. bengalensis* on the West with *M. h. chrysorrhoides* on the East we have not only many intermediate birds, which might equally well be assigned to either form, but there are many birds, the majority in fact, which can quite definitely be credited to one or the other. Thus there are in the British Museum Collection specimens from the Shan States, Yunnan, Siam, Karenni, Tenasserim, etc., some of which are labelled *chrysorrhoides*, some *nigripileus*, some *atricapillus* and some *klossi* but of the birds so labelled there are many of which it is impossible to say to which race they belong. Davison, Armstrong and others obtained birds at the same place about the same date which they had no difficulty in calling *chrysorrhoides* or *nigripileus*, yet others again are referable to either. It appears to me that all along the Siam-Burmese boundaries there is a narrow region in which there is no stable form found and where, evidently, there are such conflicting conditions in the environment that Nature has not yet had time to evolve one definite form. It is, of course, true that in all lines of demarcation between geographical races intermediate forms are the rule but in this intervening territory intermediate individuals are less common than such as can be definitely assigned to one or the other of the races in the adjoining area.
>
> In view of the many individuals which are exactly half-way between *chrysorrhoides* [= *aurigaster*] and their next-door neighbours, I propose in this work to treat all the forms as geographical races of *haemorrhous* [= *cafer*].

Study of the material before me permits me to agree with Baker's facts, but by no means with his interpretation of them. From Ceylon throughout India to eastern Burma are found a group of clinally intergradient races (*cafer*) characterized by black-to-brown ear coverts, black throat and breast, and scarlet-red under tail coverts; from southeastern China throughout Yunnan, Indochine, and Siam to eastern Burma are found a group of similarly clinally intergradient races (*aurigaster*) characterized by whitish ear coverts, whitish throat and breast, and vermilion, orange, or yellow under tail coverts. Since the members of the two groups show normal clinal intergradation everywhere else, we might expect to find, if they were truly conspecific, in western Yunnan, the Shan States, Karenni, Tenasserim, and western Siam populations in which all individuals would be more or less exactly intermediate between *cafer* and *aurigaster*. This is nowhere the case, as has been observed by Baker in the passage cited above. The idea that "Nature has not yet had time to evolve one definite form" cannot be taken seriously, since perfectly distinct races have evolved immediately east and west of the critical regions.

What in fact seems to occur in western Yunnan, the Shan States, Karenni, Tenasserim, and western Siam is, however, just what might be expected to happen if two not distantly related species make a regular practice of interbreeding and producing fertile hybrids wherever they are sympatric. Only by the adoption of this hypothesis can be explained the occurrence in a single locality on the same date of individuals that might be called *cafer*, *cafer* > *aurigaster*, *cafer* ≲ *aurigaster*, *aurigaster* > *cafer*, and

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aurigaster, when, moreover, those that might be called *cafer* > *aurigaster* or *aurigaster* > *cafer* seem to show ever possible ratio of the inheritance of one species to that of the other.

The name "*nigropileus*" (consistently misspelled by Baker) has been bestowed by Blyth (Journ. Asiat. Soc. Bengal **16** (pt. 1): 472. "May" 1847) upon certain Tenasserimese examples that seem to carry *cafer*- and *aurigaster*-inheritance in almost equal parts. This name has been applied also to somewhat similar individuals from the Shan States and western Yunnan; since these last have resulted from the union of races slightly different from the ones concerned in Tenasserim, they are not quite the same as topotypical "*nigropileus*." In "Remarks" under *Pycnonotus cafer stanfordi* (below) I have given reasons for believing that the more northern hybrids may be called "*burmanicus*," but it should be understood that I consider "*nigropileus*" and "*burmanicus*" to possess no more standing in zoological nomenclature than "*Vermivora leucobronchialis*" (Brewster), formerly used for what is now known to be a fertile hybrid between two distinct species of wood warblers.

In the discussion of the races of *P. aurigaster* to follow, I have been compelled to adopt a more or less arbitrary sequence, since no linear representation is possible that might reflect the apparent facts of their interrelationships. It seems unquestionable that *germani*, with the feathers of the pileum a pale-edged, unglossed brown, is the one most like the ancestral stock, since this character is well marked in the *juvenal* plumages of other brownish-crowned, yellow-vented forms and is at least indicated in the juvenal plumages of the black-crowned, red-vented races. To judge from the material before me, the true interrelationships are best shown by the accompanying diagram (Fig. 1).

It may be noted again that, while considerable diversity of color appears in the under tail coverts of the races of *aurigaster*, no similar variation is exhibited by *P. cafer*. How fixed is this character in the latter species is indicated by Yen's discovery in the Paris Museum of "un spécimen indien albinos ... dont les sous-caudales seules

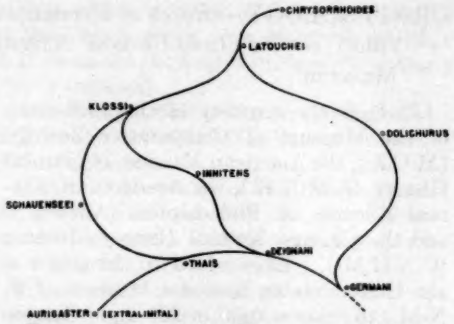

FIG. 1.—Interrelationships among races of *Pycnonotus aurigaster*.

restent rouges" (L'Oiseau et Rev. Franç. Orn., n.s., **4** (2): 303. 1934).

The following Indo-Chinese forms of the two species seem to me to deserve subspecific recognition:

A. PYCNONOTUS AURIGASTER (Vieillot)

1. **Pycnonotus aurigaster chrysorrhoides** (Lafresnaye)

Muscicapa atricapilla Vieillot, Nouveau dictionnaire d'histoire naturelle, nouv. éd., **21**: 489. May 1818 (China), not [*Muscicapa*] *Atricapilla* Linnaeus, 1766.

H[aematornis]. chrysorrhoïdes Lafresnaye, Revue Zool. **8**: 367. Oct. 1845 (Macao Island, Kwangtung Province, China).

? *Molpastes cafer insularis* Hachisuka, Orn. Soc. Japan Suppl. no. 15: 75, Oct. 30, 1939 (Nauchan, Hainan Island).

Diagnosis.—Crested pileum glossy black; feathers of the upperparts grayish brown, fringed with ashy, slightly paler on the nape and becoming ashy white on the rump; upper wing coverts colored like the back; remiges grayish brown, edged with ashy; rectrices grayish brown, becoming almost black on the apical half, the central pair narrowly, the others broadly, tipped with white; lores, feathers around the eye, chin, and sides of uppermost throat dull black; ear coverts grayish white, sometimes tinged with pale brown, especially posteriorly; underparts pale sullied gray; under tail coverts vermilion-red.

Wing length.—95.2–102.3 mm. (9 males), 91.2–93.4 mm. (3 females) 90.5–101.6 mm. (6 unsexed).

Tail length.—89.7–99.2 mm. (9 males), 82–90.1 mm. (3 females), 85.2–97 mm. (5 unsexed).

Range.—Southeastern China (Fukien, Kwangtung, and Kwangsi Provinces); eastern Tongking; northernmost Annam.

Specimens examined.—CHINA: No definite locality (1 female, 3 unsexed); Fukien Province: Kienyang (2 males), Foochow (1 male), Amoy (1 male); Kwangtung Province: Canton (1 unsexed), Macao (1 unsexed), Hongkong (2 males, 2 unsexed). TONGKING: Langson Province: Langson (1 male); Haiphong Province: Cat-Ba Island (1 male). ANNAM: Thanhhoa Province: Hoixuan (1 male, 2 females), Lunglunh (1 unsexed).

Remarks.—*Molpastes cafer insularis*, based upon one specimen, is not likely to be separable, but whether Hachisuka's name is to be placed in synonymy with *chrysorrhoides* can be decided only by examination of the type.

2. **Pycnonotus aurigaster latouchei, n. subsp.**

Type.—A. M. N. H. no. 417161, adult male, collected at Laichau (elev. 500 feet), Laichau Province, northwestern Tongking, 01 November 8, 1931, by T. D. Carter (original number 43).

Diagnosis.—From *P. a. chrysorrhoides* readily separable, especially in series, by having the feathers of the upperparts a slightly darker grayish brown, fringed with a slightly darker ashy, so that the race shows a generally deeper tone above.

Wing length.—90–103.5 mm. (23 males), 90.1–98.9 mm. (14 females).

Tail length.—81.6–95.9 mm. (20 males), 82.8–90.3 mm. (14 females).

Range. — Western Tongking; Haut-Laos; southern and western Yunnan; Southern Shan States (Kengtung State); northernmost Siam (Chiang Rai Province, where approaching *klossi*).

Specimens examined. — TONGKING: Laokay Province: Ba Nam Nhung (3 females), Baxat (1 male, 1 female); Laichau Province: Muong Moun (1 female), Paham (1 female), Laichau (2 males, 2 females). LAOS: 5° Territoire Militaire: Muong Yo (2 males), Phong Saly (1 male, 2 females). YUNNAN: Southeast: Mengtz (7 males 1 female, 1 unsexed); West: Yuankiang (2 males), Likiang Range (1 female). SOUTHERN SHAN STATES: Kengtung State: Loi Mwe (6 males, 3 females), Pang Hsang (1 male), Mong Pek (1 male, 1 female). SIAM: Chiang Rai Province: Chiang Saen Kao (1 male), Banchong Mountains (1 male), Chiang Rai (1 female).

Remarks.—That the distinguishing character of this race was noted long ago by La Touche is made evident by his choice of an unpublished manuscript name inscribed on the label of a "type" from Mengtz. Since the name in question has since been used for an Indian form of *P. cafer* I take pleasure in dedicating the new race to La Touche's memory.

3. **Pycnonotus aurigaster klossi** (Gyldenstolpe)

Molpastes atricapillus klossi "Robinson," error = Gyldenstolpe, Bull. Brit. Orn. Club **41**: 12. Nov. 9, 1920 (Doi Khun Tan, northern Siam at lat. 18°30′ N., long. 99°20′ E.); **42**: 32. Nov. 29, 1921.

Diagnosis.—A poorly defined race, distinguishable in series from the two precedent forms by having the general tone of the upperparts rather more brownish gray than grayish brown, by lesser average measurements, and by its somewhat shorter crest.

Wing length.—86.5–94.9 mm. (8 males), 83.3–90.8 mm. (12 females), 88.1–89.5 mm. (2 unsexed).

Tail length.—76.2–86.3 mm. (8 males), 72.5–85.1 mm. (12 females), 77.4–78 mm. (2 unsexed).

Range.—Tenasserim (Toungoo to Amherst Districts); Karenni; northern Siam (excepting Chiang Rai Province), south on both east and west to about lat. 16°45′ N. (where approaching *innitens* and *schauenseei*); probably adjacent parts of Laos (Vientiane Province).

Specimens examined.—TENASSERIM: Toungoo District: Thandaung (1 male); Salween District: Yunzalin River (1 male); Thaton *or* Amherst District: Thaungyin River (1 male, 1 female); Amherst District: Mepale (1 female), Myawadi (1 female). SIAM: North: Ban Rahaeng (1 female, 1 unsexed), Ban Mae Tha Khwae (1 female), Ban Wiang Tai (1 female), Ban Hua Pa Phai (1 male), Doi Chiang Dao (1 male, 1 female), *ca.* 30 miles N. of Chiang Mai (1 male), Ban San Maha Phon (1 male), Doi Suthep (1 male, 3 females) Chiang Mai (1 male, 2 females), Doi Ang Ka (1 male), Doi Khun Tan (3 males, 1 female, 1 unsexed), Ban Bo Kaeo (1 female), Ban Mae Lam Phan (1 male, 1 female).

4. **Pycnonotus aurigaster schauenseei** Delacour

Pycnonotus cafer schauenseei Delacour, Zoologica **28** (pt. 1): 29. May 4, 1943 (Ban Si Sawat, southwestern Siam at lat. 14°40′ N., long. 99°02′ E.).

Diagnosis.—A somewhat unstable race, nearest *klossi*, from which it is separable by lesser average measurements, by lesser development of the crest, by having the upperparts slightly browner in general tone, by having the light tips of the rectrices less extensive and tinged with ashy,

and by having the under tail coverts varying in hue between rosy red and red-orange.

Wing length.—82.8–92 mm. (5 males), 80.2–87.5 mm. (3 females), 92 mm. (1 unsexed).

Tail length.—74.6–87.5 mm. (5 males), 75–82.2 mm. (3 females), 84 mm. (1 unsexed).

Range.—Southwestern Siam (valley of the Mae Klong from its head [where approaching *klossi*] to about lat. 14° N.); Tenasserim (Amherst and Tavoy Districts).

Specimens examined.—SIAM: Southwest: 53 miles E. of Ban Um Phang (2 males, 1 female, 1 unsexed), Ban Si Sawat (2 males, 2 females). TENASSERIM: Amherst District: Lampha (1 female).

5. Pycnonotus aurigaster thais (Boden Kloss)

Molpastes aurigaster thais Boden Kloss, Journ. Nat. Hist. Soc. Siam 6 (3): 291. July 15, 1924 (Bangkok, central Siam at lat. 13°45′ N., long. 100° 30′ E.).

Diagnosis.—From *P. a. schauenseei* separable only by having the under tail coverts bright Cadmium Yellow (Ridgway).

Wing length.—86.3–92 mm (4 males).

Tail length.—76–78.8 mm. (3 males).

Range.—Southwestern Siam, south of the range of *schauenseei* and extending east along the coast to Bangkok.

Specimens examined.—SIAM: Southwest: Ban Tha Muang (2 males), Rat Buri (1 male), Bangkok (1 male).

6. Pycnonotus aurigaster innitens, n. subsp.

Type.—U.S.N.M. no. 307019, adult female, collected at Ban Pak Chong, eastern Siam, at lat. 14°40′ N., long. 101°25′ E., on February 7, 1925, by Hugh McC. Smith.

Diagnosis.—Nearest *P. a. schauenseei*, but differing by having the black pileum almost without gloss, especially anteriorly, where it tends to become a brownish black or blackish brown; by having the general tone of the upperparts perhaps very slightly browner; and by having the under tail coverts Scarlet-Red (1 specimen) or Peach Red (8 specimens), as these colors are understood by Ridgway.

From *P. a. klossi* separable by its less highly developed crest and by the almost wholly unglossed pileum; by having the light tips of the rectrices less extensive and tinged with ashy; by the paler reds shown by the under tail coverts; and by slightly lesser average measurements.

Wing length.—86.6–91.7 mm. (4 males), 83.4–88.3 mm. (5 females).

Tail length.—74.5–78.7 mm. (4 males), 70.6–75.3 mm. (5 females).

Range.—The southern end of the chain of hills dividing the Chao Phaya system from that of the Mae Khong (Ban Pak Chong); the southwestern portion of the plateau of eastern Siam (Ban Bua Yai); the country between this plateau and "Southeastern Siam" (Nakhon Nayok, Kabin Buri); southeastern Siam (Ban Si Racha).

Specimens examined.—SIAM: Southeast: Ban Bua Yai (1 female), Ban Pak Chong (1 male, 1 female), Nakhon Nayok (2 males), Kabin Buri (1 female), Ban Si Racha (1 male, 2 females).

Remarks.—As *P. a. schauenseei* represents the intergrade between red-vented *klossi* and yellow-vented *thais*, this form represents the corresponding intergrade on the other side of the central Siamese plain between *klossi* and the yellow-vented *deignani*. *Pycnonotus a. innitens* seems to occur only in isolated populations, and it is of especial interest to find that along a limited stretch of the coast of the Gulf of Siam one finds yellow-vented *thais* at Bangkok, red-vented *innitens* at Ban Si Racha, and yellow-vented *deignani* at Chanthaburi.

7. Pycnonotus aurigaster deignani Delacour

Pycnonotus cafer deignani Delacour, Zoologica **28** (pt. 1): 29. May 4, 1943 (Chanthaburi, southeastern Siam at lat. 12°35′ N., long. 102°05′ E.).

Diagnosis.—From *P. a. innitens* separable only by having the under tail coverts Primuline Yellow (Ridgway).

From *P. a. thais* separable by having the black pileum almost without gloss, especially anteriorly where it tends to become a blackish brown.

Wing length.—84.8–90.8 mm. (4 males), 81.4–86.4 mm. (2 females).

Tail length.—72.8–78.9 mm. (4 males), 69.8–75.2 mm. (2 females).

Range.—Southeastern Siam (Chanthaburi).

Specimens examined—SIAM: Southeast: Chanthaburi (6 males, 2 females).

8. Pycnonotus aurigaster germani (Oustalet)

Ixus Germani Oustalet, Bull. Soc. Philom. Paris, ser. 7, **2** (1): 54. 1878 (Saigon, Cochinchine).

Diagnosis.—Nearest *P. a. deignani*, but easily separable in the adult by having the pileum almost devoid of a crest and with each brownish-black or blackish-brown feather narrowly edged

with a lighter brown (exactly as in the immature of *deignani*).

Wing length.—88–92 mm. (10 males), 84–88.5 mm. (14 females), 86–89.2 mm. (2 unsexed).

Tail length.—74.6–81.2 mm. (10 males), 73.1–78 mm. (13 females), 76.1–79.2 mm. (2 unsexed).

Range. — Cochinchine; southern Annam; Bas-Laos; extreme eastern Siam (along the Mae Khong in Ubon Province).

Specimens examined.—SIAM: East: Ban Chanuman (2 males, 5 females), Ban Khulu (2 males, 1 female). BAS-LAOS: Pakse Province: Pakse (1 male); Saravane Province: Phu Tongtoul (1 female). ANNAM: Phanrang Province: Krongpha (2 males), between Bellevue and Daban (1 female), Fimnon (1 male, 5 females, 2 unsexed), Daban (1 male), Dran (2 males, 2 females), Dalat (1 female), between Dalat and Ban Methuot (2 females), 35 kilometers south of Dalat (2 males), 50 kilometers southeast of Dalat (2 males).

9. **Pycnonotus aurigaster dolichurus,** n. subsp.

Type.—C.N.H.M. no. 79300, adult male, collected at Phuoc, Quangtri Province, central Annam, on January 25, 1929, by J. Van Tyne (original number 68).

Diagnosis.—Nearest *P. a. chrysorrhoides* (which reaches northern Annam), but separable by shorter wing length and by having the black pileum virtually unglossed.

From *P. a. innitens*, which it resembles in the coloration of the under tail coverts, distinguishable by its more highly developed crest, by longer wing and much longer tail measurements, and by having the light tips of the rectrices broader and whiter.

Wing length.—92.3–95.3 mm. (6 males), 86.7–87 mm. (2 females).

Tail length.—85.5–99.7 mm. (6 males), 80.6–83.1 mm. (2 females).

Range.—Central Annam.

Specimens examined.—ANNAM: Quangtri Province: Phuoc (6 males, 2 females).

Remarks.— *P. a. dolichurus* represents the intermediate population between red- and yellow-vented birds along the coast of Annam, as *P. a. innitens* does in southeastern Siam and *P. a. schauenseei* in southwestern Siam. It is, however, a considerably larger form than either of the other two.

B. PYCNONOTUS CAFER (Linnaeus)

1. **Pycnonotus cafer stanfordi,** n. subsp.

Type.—A.M.N.H. no 409420, adult male, collected at Taro *or* Dalu (lat. 26° 20′ N., long. 96° 10′ E.), Upper Chindwin District, Sagaing Division, Burma, on February 10, 1935, by members of the Vernay-Hopwood Chindwin Expedition (original number 321).

Diagnosis.—Similar to *Pycnonotus aurigaster latouchei* (with which westerly it is cohabitant), but differing by having the dark centers of the feathers of the upperparts more clearly defined; the ear coverts hair brown; the chin and throat black, this color changing to blackish brown on the breast, of which the lateral and posterior feathers are broadly fringed with ashy; the undertail coverts a deeper Scarlet-Red (Ridgway).

Wing length.—96.8-105.7 mm. (15 males), 94–97.2 mm. (4 females), 98.5 mm. (1 unsexed).

Tail length.—81–97.2 mm. (15 males), 84.2–89.3 mm. (3 females), 86.4 mm. (1 unsexed).

Range.—Northern Burma (Pakkoku, Lower Chindwin, Upper Chindwin, Myitkyina, Bhamo Districts); Yunnan (west); Northern Shan States

Specimens examined.—YUNNAN: West: Manhsien (1 female), Tengyueh (4 males, 2 females). BURMA: Myitkyina District: Washaung (1 female), Chipwi (1 male), Seniku-Sh'ngaw road (1 male), Lonkin (1 male); Bhamo District: Bhamo (2 males); Upper Chindwin District: Taro (2 males), Namyaseik (1 male); Lower Chindwin District: Aingma (1 male), "Moungon" (1 male); Pakkoku District: Kyundaw (1 unsexed). NORTHERN SHAN STATES: Hispaw State: Chaungzon (1 male).

Remarks.—This race, named in honor of the well-known authority on Burmese birds, J. K. Stanford, has, by the most recent writers (Stanford and Mayr Ibis, 1941: 103; Stanford and Ticehurst, Ibis, 1938: 214; Mayr, *ibid.*: 291), been called *burmanicus* of Bowdler Sharpe (Catalogue of the birds in the British Museum **6:** 125. 1882).

Sharpe designated no specimen as type, but stated that the form ranged "from Cachar into Pegu," and listed six examples from northeastern Burma, western Yunnan, and Pegu (no British Museum bird from Cachar).

Since series before me from Cachar, northeastern Burma, western Yunnan, and Pegu show that Sharpe had combined under one name no

less than three geographical races and one interspecific hybrid, I have been compelled to decide, on the basis of his written description, to which of these the name must be applied.

Sharpe's statement, "the hinder neck coloured like the back, but more distinctly ashy," immediately removes from consideration the population of Cachar, which has the hind neck darker than the back, nigrescent and not trenchantly defined from the pileum.

Other statements, "Above light brown ... the lower back and rump uniform ashy ... the hinder neck coloured like the back, but more distinctly ashy ... ear-coverts ashy brown," further restrict the use of the name to birds of northeastern Burma and western Yunnan, where, however, the problem is complicated by the presence of hybrids. But the further statement, "fore neck and breast light brown," seems to show without question that one of these hybrids must be considered typical of *burmanicus*, since the full-blooded birds that I have named *stanfordi* have this area ranging from black to blackish brown, while the hybrids, in fact, show a color that might well be described as "light brown." These hybrids have in the past been called "*nigropileus*," but they are considerably larger and more richly colored everywhere than topotypical "*nigropileus*" from Tenasserim, and, if it should prove desirable, the name "*burmanicus*" may be used for them, although, as I have stated in my introductory remarks, these names should not be thought to possess standing in zoological nomenclature.

It may be suggested that I have for legalistic reasons discarded a name previously considered available, but it seems certain that careful comparison of specimens with Sharpe's description will show that there is no alternative action. In naming the population of northeastern Burma I have selected a type locality well without the area in which hybrid individuals are ever likely to occur.

2. **Pycnonotus cafer melanchimus**, n. subsp.

Type.—A.M.N.H. no. 568717, adult male, collected at Rangoon, Rangoon Town District, Pegu Division, Burma, on January 2, 1906, by H. H. Harington (original number 279), *ex* Rothschild Museum.

Diagnosis.—Nearest *P. c. stanfordi*, but distinguishable by having the feathers of the upperparts with darker centers and more narrowly edged with ashy, so that the general tone of the back is deeper; the ear coverts a deeper hair brown; the blackish-brown coloration of the anterior underparts extending onto the abdomen, with resultant decrease of the ashy-white area below; possibly also by having the white tips to the rectrices less extensive in unworn plumage.

Wing length.—93.8–99 mm. (4 males), 87.2 mm. (1 female).

Tail length.—85.1–90.4 mm. (4 males), 79.2 mm. (1 female).

Range.—Sourthern Burma (Thayetmyo, Pegu, Rangoon Town Districts), perhaps restricted to the country between the Irrawaddy and Sittang Rivers, so far as this lies south of *ca.* lat. 20° N.

Specimens examined.—BURMA: Thayetmyo District: Kyaukpadaung (1 male); Pegu District: Zaingganaing (1 male); Rangoon Town District: Rangoon (2 males, 2 females).

Remarks.—A single specimen (male?) from lat. 19° 25′ N., long. 94° 40′ E. (near Mindon at the eastern foot of the Arakan Yoma in the Thayetmyo District) agrees very well in color with *P. c. stanfordi*, but has the narrow tail tips and small measurements of *melanchimus* (wing: 90.2 mm.; tail: 80.3 mm.). For the present this individual cannot be identified to subspecies.

3. **Pycnonotus cafer primrosei**, n. subsp.

Type.—U.S.N.M. no. 253767, adult male, collected at the Surma Tea Estate, southern Sylhet District, Surma Valley and Hill Division, Assam Province, India, on January 1, 1900, by A. M. Primrose.

Diagnosis.—Near *P. c. standfordi*, but easily distinguished therefrom and from all other precedent forms by having the nape and sometimes the upper back black or at least blackish, so that the pileum is not at all clearly defined from the mantle.

Near *P. c. pygaeus* (see below), but distinguishable from it by having the ear coverts hair brown of the same tone as in *P. c. stanfordi*.

Wing length.—95–104 mm. (8 males), 95.9–106 mm. (4 females).

Tail length.—82.7–94.2 mm. (7 males), 83–98.1 mm. (4 females).

Range.—Assam (Goalpara, Garo Hills, Sylhet, Cachar, and probably still other districts south of the Brahmaputra River).

Specimens examined.—ASSAM: Goalpara District: Goalpara (1 male); Garo Hills District: Tura (2 females); Sylhet District: Surma Tea Estate (1 male), Rena Tea Estate (1 female); Cachar District: Laisung (1 male), Mahur (1

male), Guilang (1 male), Gunjong (3 males, 1 female).

Remarks.—Birds from the Goalpara and Garo Hills Districts are approaching *pygaeus*; a single unsatisfactory specimen from the Patkai Hills seems to be nearer *stanfordi* than *primrosei*.

This race is named in honor of the collector, A. M. Primrose.

4. **Pycnonotus cafer pygaeus** (Hodgson)

[*Ixos*] *pygæus* Hodgson, *in* J. E. Gray, Zoological Miscellany, no. 3: 84. "June" 1844 (Nepal).

P[*ycnonotus*]. *bengalensis* Blyth, Journ. Asiat. Soc. Bengal **14** (pt. 2): 566 and footnote. Aug. 1845 (Bengal).

Ixos cafer? v[el]. *pygmæus* 'Hodgs." J. E. Gray, Catalogue of the specimens and drawings of Mammalia and birds of Nepal and Thibet: 89. 1846 (Nepal).

I[*xos*]. *pygaeus* "Hodgson" Bonaparte, Conspectus generum avium **1**: 265. 1850 ("ex Him. Assam, Bengal").

Pycn[*onotus*]. *pseudocafer* "Blyth" Bonaparte, Conspectus generum avium **1**: 265. 1850. *Nomen nudum*, in synonymy with *I*[*xos*]. *pygaeus* "Hodgs." Bonaparte ("ex Him. Assam, Bengal").

Diagnosis.—Nearest *P. c. primrosei*, from which it is certainly distinguishable only by having the ear coverts a deeper hair brown of the same tone as in *P. c. melanchimus*.

Wing length.—98.2–104.3 mm. (6 males), 92.4–103.8 mm. (6 unsexed).

Tail length.—88.2–96.7 mm. (4 males), 86.5–93.6 mm. (5 unsexed).

Range.—Nepal; Sikkim; eastern United Provinces: Bihar; Bengal; Assam (hills north of the Brahmaputra River); Fiji Islands (introduced into Viti Levu).

Specimens examined.—NEPAL: No definite locality (1 unsexed); SIKKIM: No definite locality (2 unsexed). "INDIA": No definite locality (1 unsexed). UNITED PROVINCES: Kheri District: North Kheri Forest (1 male); Partabgarh District: Partabgarh (1 male); BENGAL: No definite locality (1 unsexed); Darjiling District: Sangsir (1 male), Siliguri (1 male), Mangpu (2 males, 1 unsexed). FIJI ISLANDS: Viti Levu: no definite locality (1 female), Rewa River, 30 miles inland (1 male), 4 miles from Suva (1 unsexed).

Remarks.—Under [*Ixos*] *pygæus* Hodgson, 1844, we find "*Ixos cafer?* v[el]. *pygœus*, 207." This seems by the narrowest margin to validate the name from 1844; if, however, the reference is rejected, this form must be called *Pycnonotus cafer bengalensis* Blyth, 1845.

PROCEEDINGS OF THE ACADEMY

428TH MEETING OF BOARD OF MANAGERS

The 428th meeting of the Board of Managers, held in the Cosmos Club, May 16, 1949, was called to order at 8:05 P.M. by the President, F. H. H. ROBERTS, JR. Others present were: F. B. SILSBEE, H. S. RAPPLEYE, H. A. REHDER, ALAN STONE, W. W. DIEHL, F. M. DEFANDORF, C. L. GAZIN, F. E. JOHNSTON, F. D. ROSSINI, J. B. REESIDE, JR., W. A. DAYTON, C. A. BETTS, R. S. DILL, A. O. FOSTER, O. B. FRENCH, and, by invitation, H. E. MCCOMB, J. L. SHERESHEFSKY.

The chairman of the Committee on Membership, H. E. MCCOMB, presented eight nominations for resident membership.

The chairman of the Committee on Grants-in-Aid for Research, J. L. SHERESHEFSKY, announced that funds available for grants-in-aid from the American Association for the Advancement of Science now amounted to $596.50, accumulated as follows: $163.00 from 1947, $213.00 from 1948, and $220.50 for the current year 1949. It was noted that the $163.00 from 1947 must be specifically committed by December 31, 1949, or this amount would be lost to the Academy for this purpose. The chairman of the committee recommended that announcement be made of the availability of these funds to research, specifically that the Secretary by letter so inform the various affiliated societies and that published announcement be made in the July and September issues of the JOURNAL. It was further stipulated that the final date for receiving applications this year would be November 1. The recommendation was accepted by the Board.

The Secretary announced the following deaths:

WHITMAN CROSS, former director of the U. S. Geological Survey, original member of the Academy, on April 20, 1949 (elected March 17, 1898); ORATOR F. COOK, formerly with the Bureau of Plant Industry, U. S. Department of Agriculture, original member, on April 23, 1949 (elected March 17, 1898); PHILIP S. SMITH, formerly with the U. S. Geological Survey, on May 10, 1949 (elected January 18, 1912).

The Custodian and Subscription Manager of Publications, Harald A. Rehder, announced that the Academy had recently received an almost complete set of the Journal, lacking but 21 num-

bers, from Fred H. Moffit. It was also announced that 7 copies of the monograph had been sold.

The President announced receipt of the following letter from Frank Thone, the Academy's representative on the Joint Committee on Press Relations:

> Pursuant to our recent telephonic discussions of the status of the Science Calendar which Mr. Darnell has been preparing for local newspapers, he has written me a letter to place on record his transactions with the Council, and his intention of carrying on the program by himself—with, of course, the little assistance I am able to give him.
>
> This is for your information, and transmittal to Dr. Setzler for his files.
>
> Mr. Darnell adds, in a hand-written note: "I find we have sufficient funds to carry us through June of this year."

The Secretary was then requested by the President to read the letter which Frank Thone received from Richard C. Darnell.

After some discussion of the background of the subject of Mr. Darnell's letter, it was proposed and approved that a conference be arranged between the President or a committee from the Academy and the D. C. Council of Engineering and Architectural Societies to discuss ways and means of continuing the Science Calendar.

The meeting was adjourned at 8:58 P.M.

C. LEWIS GAZIN, *Acting Secretary.*

Obituary

RICHARD CHACE TOLMAN was born in West Newton, Mass., on March 4, 1881. His undergraduate college work was undertaken at Massachusetts Institute of Technology, and he also obtained there in 1910 the degree of Ph.D. During the preceding three years he was a member of that now famous group of physical chemists that the late Prof. A. A. Noyes gathered around him. This group included such notables as G. N. Lewis, E. W. Washburn, W. C. Bray, John Johnston, and others, all of whom through the inspiring example of Professor Noyes committed themselves to physical chemistry as their career and made outstanding contributions in that field.

After leaving M.I.T., Dr. Tolman held positions successively on the faculties of the Universities of Michigan, Cincinnati, California, and Illinois. During World War I he entered the Chemical Warfare Service with the rank of major; and following the end of the war was associate director and then director of the Fixed Nitrogen Research Laboratory. In 1922 he went to the California Institute of Technology as professor of physical chemistry and mathematical physics; and in 1935 became dean of the graduate school, a position he held until his death on September 5, 1948.

During World War II he was chosen by Dr. Vannevar Bush to be a member of the newly constituted National Defense Research Committee, and he functioned as vice chairman of that important body until its dissolution at the war's end. He served as an adviser to Maj. Gen. Leslie Groves in connection with the famous Manhatten Project; and in 1946 he accepted an appointment as scientific adviser to the United States representative to the United Nations Atomic Energy Commission.

Besides being a member of the Washington Academy of Sciences, Dr. Tolman was a member or a fellow of many other scientific societies, including the National Academy of Sciences, American Chemical Society, American Philosophical Society, American Physical Society, Optical Society of America, American Academy of Arts and Sciences, and American Association for the Advancement of Science.

He is best known for his investigations on colloids, relativity, similitude, the mass of the electron, the nature of the fundamental quantities of physics, the partition of energy, the behavior of smokes, the electric discharge in gases, the reactions of nitrogen compounds, the rate of chemical reaction, the specific heat and entropy of gases, the quantum theory, statistical mechanics, relativistic thermodynamics, cosmology, ionization, and metallic conductors.

He is author of many articles published in various scientific journals and of several books including the following: *The theory of the relativity of motion*, published in 1917; *Statistical mechanics with applications to physics and chemistry*, published in 1927; *Relativity, thermodynamics and cosmology*, published in 1934; and *The principles of statistical mechanics*, 1938.

Dr. Tolman's passing is a great loss to the scientific world and is felt keenly by all who knew him. He was a broad-minded scholar, a great teacher, and an outstanding investigator. Above all, he was endowed with those qualities of tact, sympathy, and understanding that endeared him to his students and his colleagues.

LEASON H. ADAMS.